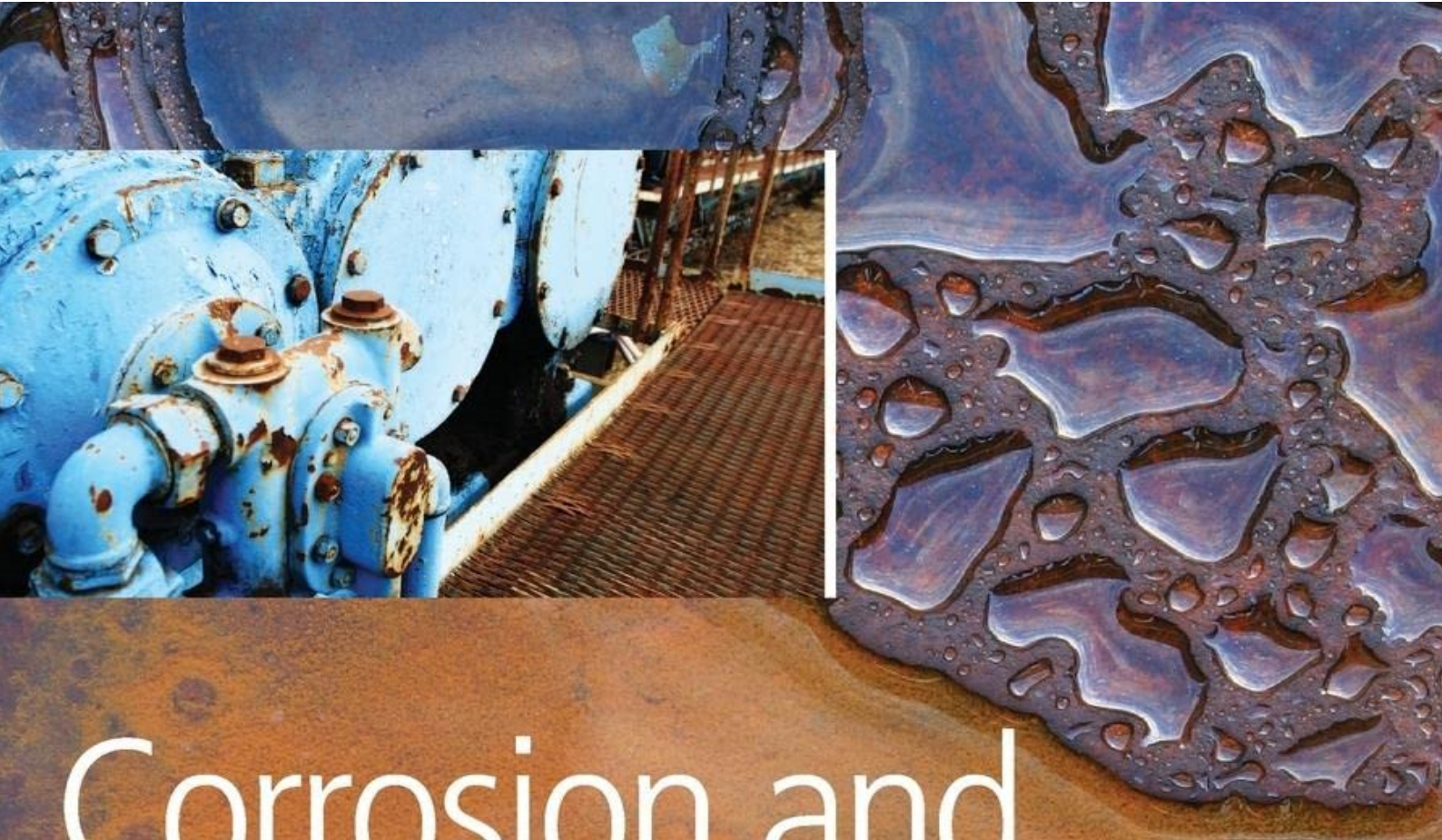


Corrosion and Materials Selection

A Guide for the Chemical and Petroleum Industries



Alireza Bahadori

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A Guide for the Chemical and Petroleum Industries

Alireza Bahadori

School of Environment, Science and Engineering,
Southern Cross University, Australia

WILEY

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Dedicated to the loving memory
of my parents, grandparents,
and to all who contributed
so much to my work
over the years

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About the Author

Alireza Bahadori, PhD, is a research staff member in the School of Environment, Science and Engineering at Southern Cross University, Lismore, NSW, Australia. He received his PhD from Curtin University, Perth, Western Australia.

During the past 20 years, Dr Bahadori has held various process and petroleum engineering positions and has been involved in many large-scale projects at the National Iranian Oil Co. (NIOC), Petroleum Development Oman (PDO), and Clough AMEC PTY LTD. He is the author of around 250 articles and 12 books, published by prestigious publishers such as John Wiley & Sons, Elsevier, Springer, and Taylor & Francis.

Dr Bahadori is the recipient of the highly competitive and prestigious Australian Government's Endeavour International Postgraduate Research Award as part of his research in the oil and gas area. He also received a top-up award from the State Government of Western Australia through Western Australia Energy Research Alliance (WA:ERA) in 2009. Dr Bahadori serves as a member of the editorial board and a reviewer for a large number of journals. He was honoured by Elsevier as the outstanding author of Journal of Natural Gas Science and Engineering in 2009.

Preface

Metallic corrosion is costly. Several billion dollars annually in the USA, and about one-third of that is noted as *avoidable corrosion*, a cost that could be eliminated if proper corrosion protection methods were in place.

Today, there are a great deal of construction materials available, varying from metallic to non-metallic. There are also a large number of factors to be taken into consideration when selecting a material for a given application.

Factors that influence corrosion consideration in material selection are distinct from those that interact in a more complex fashion. For example, "application" influences selection because the type of process, and the variables during operation etc., will define whether a material can be used for the intended purpose or not. On the other hand mechanical and metallurgical properties are not uniquely defined for all environments. For example, if the material is to be used at low temperature then embrittlement can be a serious problem.

These considerations have a direct influence on corrosion consideration in material selection. However, when there is discrepancy amongst sections of this book, or between this and other disciplines regarding selection of materials, other priorities, such as client preference, in-house experience, and specific industry standards, should also be observed.

This book covers corrosion considerations in the selection of materials specifically used in the oil, gas, chemical and petrochemical industries. It provides the necessary tools for the design stage of a system, in order to avoid or minimize corrosion hazards technically, economically and safely during the designed life of such a system. Proper corrosion control of structures and units is most effectively and economically begun during the design stage.

Various forms of corrosion and prevention methods are discussed in this book.

It also deals with the control of corrosive environments by inhibitors, general requirements for the petroleum and chemical industries, and utility systems such as cooling water, boiler water systems etc.

Finally it deals with monitoring internal corrosion. It provides guidance for on-line monitoring of internal corrosion in plants associated with the oil, gas and chemical industries, and guidance on laboratory monitoring and evaluation of corrosion inhibitors. The book also covers experiments on the corrosion behaviour of high-alloy tubular materials in inhibited acidizing conditions.

Metallic corrosion is costly. However, the cost of corrosion is not just financial. Beyond the huge direct outlay of funds to repair and/or replace corroded and/or decaying structures are the indirect costs (natural resources, potential hazards, and lost opportunities). When a project is constructed with a material not able to survive its environment for the length of the designed life, natural resources are needlessly consumed to continually repair and maintain the structure. Wasting natural resources is a direct contradiction of the growing need for sustainable development to benefit future generations.

In addition to the waste of natural resources, facilities that cannot sustain their environment can lead to hazardous situations. Accidents caused by corroded structures can lead to huge safety concerns, loss of life and resources, and more. One failed pipeline, bridge collapse, or other catastrophe is one too many, and leads to huge indirect costs (more traffic delays, loss of business, etc.) and public outcry. Depending on which market sector (industrial, infrastructure, commercial, etc.) is being considered, these indirect costs may be as high as five to ten times the direct cost.

Acknowledgements

I would like to thank the editorial and production team, Rebecca Stubbs, Emma Strickland, and Sarah Keegan of John Wiley & Sons for their editorial assistance.

1

Fundamentals of Corrosion in the Oil, Gas, and Chemical Industries

The petroleum and chemical industries contain a wide variety of corrosive environments; many are unique to these industries. Thus it is convenient to group all these environments together. Corrosion problems occur in at least three general areas: (1) production, (2) transportation and storage, and (3) operations.

Oil and gas production operations consume a tremendous amount of iron and steel pipe, tubing, pumps, valves, and sucker rods. Leaks cause loss of oil and gas, and also permit infiltration of water and silt, thus increasing corrosion damage. Saline water and sulfides are often present in oil and gas wells and corrosion occurs both inside and outside the casing. Surface equipment is subject to atmospheric corrosion.

What follows is a simple explanation of how corrosion occurs, the different types, and how problems can be solved.

We have all seen corrosion and know that the process produces a new and less desirable material from the original metal and can result in a loss of function of the component or system. The corrosion product we see most commonly is the rust which forms on the surface of steel.

$$\text{Steel} \rightarrow \text{Rust} \tag{1.1}$$

For this to happen the major component of steel, iron (Fe) at the surface of a component undergoes a number of simple changes. Firstly, the iron atom can lose some electrons and become a positively charged ion.

$$\text{Fe} \rightarrow \text{Fe}^{n+} + \text{n electrons} \tag{1.2}$$

This allows it to bond to other groups of atoms that are negatively charged. We know that wet steel rusts to give a variant of iron oxide, so the other half of the reaction must involve water (H_2O) and oxygen (O_2), something like this:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1.3}$$

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This makes sense as we have a negatively charged material that can combine with the iron and electrons produced in the first reaction. We can, for clarity, ignore the electrons and write

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

iron + water with oxygen → iron hydroxide dissolved in it (1.4)

Oxygen dissolves quite readily in water and because there is usually an excess of it, reacts with the iron hydroxide.

$$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3.H_2O$$

iron hydroxide + oxygen → water + hydrated iron oxide (brown rust) (1.5)

This series of steps tells us a lot about the corrosion process:

1. Ions are involved and need a medium to move in (usually water).
2. Oxygen is involved and needs to be supplied.
3. The metal has to be willing to give up electrons to start the process.
4. A new material is formed and this may react again or could protect the original metal.
5. A series of simple steps are involved and a driving force is needed to achieve them.
6. The most important fact is that interfering with the steps allows the corrosion reaction to be stopped or slowed to a manageable rate.

1.1 Uniform Corrosion

Uniform corrosion, as the name suggests, occurs over the majority of the surface of a metal at a steady and often predictable rate. Although it is unsightly, its predictability facilitates easy control, the most basic method being to make the material thick enough to function for the lifetime of the component. Uniform corrosion can be slowed or stopped in five basic ways:

1. Slow down or stop the movement of electrons:
   - **(a)** Coat the surface with a non-conducting medium such as paint, lacquer or oil
   - **(b)** Reduce the conductivity of the solution in contact with the metal, an extreme case being to keep it dry
   - **(c)** Wash away conductive pollutants regularly
   - **(d)** Apply a current to the material (see cathodic protection).
2. Slow down or stop oxygen from reaching the surface. This is difficult to do completely, but coatings can help.
3. Prevent the metal from giving up electrons:
   - **(a)** Use a more corrosion-resistant metal higher in the electrochemical series,
   - **(b)** Use a sacrificial coating that gives up its electrons more easily than the metal being protected
   - **(c)** Apply cathodic protection
   - **(d)** Use inhibitors.

4. Select a metal that forms an oxide that is protective and stops the reaction.
5. Control and consideration of environmental and thermal factors is also essential.

1.2 Localized Corrosion

The consequences of localized corrosion can be a great deal more severe than uniform corrosion, generally because the failure occurs without warning and after a surprisingly short period of use or exposure. Application of the five basic principles needs greater thought and insight.

1.2.1 Galvanic Corrosion

This can occur when two different metals are placed in contact with each other and is caused by the greater willingness of one to give up electrons than the other. Three special features of this mechanism need to operate for corrosion to occur:

- The metals need to be in contact electrically.
- One metal needs to be significantly better at giving up electrons than the other
- An additional path for ion and electron movement is necessary.

Prevention of this problem is based on ensuring that one or more of the three features do not exist:

- Break the electrical contact using plastic insulators or coatings between the metals.
- Select metals close together in the galvanic series.
- Prevent ion movement by coating the junction with an impermeable material, or ensure the environment is dry and that liquids cannot be trapped.

1.2.2 Pitting Corrosion

Pitting corrosion occurs in materials that have a protective film, such as a corrosion product or a coating. When this breaks down, the exposed metal gives up electrons easily and the reaction initiates tiny pits with localized chemistry supporting rapid attack. Control can be ensured by:

- selecting a resistant material,
- ensuring a high enough flow velocity of fluids in contact with the material or
- frequent washing,
- control of the chemistry of fluids and use of inhibitors,
- use of a protective coating,
- maintaining the material's own protective film.

Note: Pits can be crack initiators in stressed components or those with residual stresses resulting from forming operations. This can lead to stress corrosion cracking.

1.2.3 Selective Attack

This occurs in alloys such as brass, when one component or phase is more susceptible to attack than another and corrodes preferentially, leaving a porous material that crumbles. It is best avoided by selection of a resistant material, but other means can be effective such as:

- Coating the material
- Reducing the aggressiveness of the environment
- Use of cathodic protection.

1.2.4 Stray Current Corrosion

When a direct current flows through an unintended path, the flow of electrons supports corrosion. This can occur in soils, and flowing or stationary fluids. The most effective remedies involve controlling the current by:

- insulating the structure to be protected or the source of current,
- earthing sources and/or the structure to be protected,
- applying cathodic protection,
- using sacrificial targets.

1.2.5 Microbial Corrosion

This general class covers the degradation of materials by bacteria, molds, and fungi, or their by-products. It can occur by a range of actions, such as:

- Attack on the metal or protective coating by acid by-products, sulfur, hydrogen, sulfide or ammonia
- Direct interaction between the microbes and metal under attack.

Prevention can be achieved by:

- selection of resistant materials,
- frequent cleaning,
- control of the chemistry of the surrounding medium and removal of nutrients,
- use of biocides,
- cathodic protection.

1.2.6 Intergranular Corrosion

This is preferential attack on the grain boundaries of the crystals that form the metal. It is caused by the physical and chemical differences between the centers and the edges of the grain.

It can be avoided by:

- selection of stabilized materials,
- control of heat treatments and processing to avoid susceptible temperature range.

1.2.7 Concentration Cell Corrosion (Crevice)

If two areas of a component in close proximity differ in the amount of reactive constituent available, the reaction in one of the areas is speeded up. An example of this is crevice corrosion, which occurs when oxygen cannot penetrate a crevice and a differential aeration cell is set up. Corrosion occurs rapidly in the area with less oxygen. The potential for crevice corrosion can be reduced by:

- avoiding sharp corners and designing out stagnant areas,
- use of sealants,
- use of welds instead of bolts or rivets,
- selection of resistant materials.

1.2.8 Thermogalvanic Corrosion

Temperature changes can alter the corrosion rate of a material and a good rule of thumb is that a 10 °C rise doubles the corrosion rate. If one part of component is hotter than another, the difference in the corrosion rate is accentuated by the thermal gradient and local attack occurs in a zone between the

maximum and minimum temperatures. The best method of prevention is to design out the thermal gradient or to supply a coolant to even out the difference.

1.2.9 Corrosion Caused By Combined Action

This is corrosion accelerated by the action of fluid flow, sometimes with the added pressure of abrasive particles in the stream. The protective layers and corrosion products of the metal are continually removed, exposing fresh metal to corrosion. Prevention can be achieved by:

- reducing the flow rate and turbulence,
- use of replaceable or robust linings in susceptible areas,
- avoiding sudden changes of direction,
- streamlining or avoiding obstructions to the flow.

1.2.10 Corrosion Fatigue

The combined action of cyclic stresses and a corrosive environment reduce the life of components below that expected by the action of fatigue alone. This can be reduced or prevented by:

- coating the material,
- good design that reduces stress concentration,
- avoiding sudden changes of section,
- removing or isolating sources of cyclic stress.

1.2.11 Fretting Corrosion

This is caused by relative motion between two surfaces in contact by a stick–slip action resulting in breakdown of protective films or welding at the contact areas, allowing other corrosion mechanisms to operate. Prevention is possible by:

- designing out vibrations,
- lubrication of metal surfaces,
- increasing the load between the surfaces to stop the motion,
- surface treatments to reduce wear and increase the friction coefficient.

1.2.12 Stress Corrosion Cracking

The combined action of a static tensile stress and corrosion forms cracks and eventually leads to catastrophic failure of the component. This is specific to a metal material paired with a specific environment. Prevention can be achieved by:

- reducing the overall stress level and designing out stress concentrations,
- selection of a suitable material not susceptible to the environment,
- designing to minimize thermal and residual stresses,
- developing compressive stresses in the surface the material,
- use of a suitable protective coating.

1.2.13 Hydrogen Damage

A surprising fact is that hydrogen atoms are very small and hydrogen ions even smaller and can penetrate most metals. Hydrogen, by various mechanisms, embrittles a metal, especially in areas

of high hardness causing blistering or cracking particularly in the presence of tensile stresses. This problem can be prevented by:

- using a resistant or hydrogen-free material,
- avoiding sources of hydrogen, such as cathodic protection, pickling processes, and certain welding processes,
- removal of hydrogen within the metal by baking.

Corrosion control measures should be implemented during the design stage of petroleum and chemical plants and include:

- Proper design
- Proper material selection
- Proper process that involves reduced temperature, low concentration of critical corrosive species, reduced flow velocity, oxygen elimination, etc.
- Proper protective coatings and linings, especially for refractories.

For practical purposes, corrosion in oil, gas, petrochemical, and chemical plants can be classified into low-temperature corrosion and high temperature corrosion. Low temperature corrosion occurs below 260 °C in the presence of water. High temperature corrosion takes place above 260 °C. The presence of water is not necessary in this case because corrosion occurs by direct reaction between the metal and the environment.

1.3 Low-Temperature Corrosion

Most corrosion problems are not caused by hydrocarbons, but by various inorganic compounds such as water, hydrogen sulfide, hydrochloric acid, hydrofluoric acid, sulfuric acid, and caustic. There are two principal sources of these compounds, feed-stock contaminants and process chemicals.

1.3.1 Low-Temperature Corrosion by Feed-Stock Contaminants

In this case, the cause of refinery corrosion is the presence of contaminants in the crude oil as it is processed. Corrosive hydrogen chloride evolves in crude preheat furnaces from relatively harmless magnesium and calcium chlorides entrained in crude oil. In petrochemical plants, certain corrosives may have been introduced from upstream refinery and other process operations. Other corrosives can form from corrosion products after exposure to air during shut-down; polythionic acids fall into this category. Corrosive contaminants are as follows:

- Air
- Water
- Hydrogen sulfide
- Hydrogen chloride
- Nitrogen compounds
- Sour water
- Polythionic acids.

1.3.1.1 Air

During shut-down most plant equipment is exposed to air. Air also can enter the suction side of pumps if seals are not tight. In general, the air contamination of hydrocarbon streams is more detrimental with regard to fouling than corrosion. However, air contaminant has been cited as a cause of accelerated

corrosion in vacuum towers and vacuum transfer lines, and accelerated overhead corrosion of crude distillation towers.

1.3.1.2 Water

The water content of crude oils and water originating from stripping steam in fractionation towers hydrolyzes certain inorganic chlorides to hydrogen chloride, and is responsible for various forms of corrosion in fractionation tower overhead systems. It is good practice to keep equipment dry in order to minimize corrosion.

A combination of moisture and air enters into storage tanks during normal breathing as a result of pumping and changes in temperature. Corrosion of tank bottoms occurs mostly with crude oil tanks, and is caused by water and salt entrained in the crude oil. A layer of water usually settles out and can become highly corrosive.

1.3.1.3 Hydrogen Sulfide

Hydrogen sulfide is the main constituent of refinery sour water and can cause severe corrosion problems in the overhead systems of certain fractionation towers, in hydrocracker and hydrotreater effluent streams from vapor recovery of fluid catalytic cracking (FCC) units, in sour water stripping units and in sulfur recovery units. Carbon steel has fairly good resistance to aqueous sulfide corrosion because a protective film of FeS is formed to avoid hydrogen stress cracking (sulfide cracking); hard welds (above 200 HB) must be avoided, through suitable post-weld heat treatment, if necessary.

Excessive localized corrosion in vessels can be resolved by selective lining with alloy 400 (N04400), but this can be less resistant than carbon steel to aqueous sulfide corrosion at temperatures above 150 °C. If significant amounts of chlorides are not present, lining vessels with Type 405 (S40500) or Type 304 (S30400) stainless steel can be considered.

Recently titanium Grade 2 (R50400) tubes have been used as replacements for carbon steel tubes to control aqueous sulfide corrosion in heat exchangers. Hydrogen sulfide is present in some feed stocks handled by petrochemical plants. During processing at elevated temperatures, hydrogen sulfide is also formed by the decomposition of organic sulfur compounds that are present.

1.3.1.4 Hydrogen Chloride

In refineries, corrosion by hydrogen chloride is primarily a problem in crude distillation units, and to lesser degree in reforming and hydrotreating units. In petrochemical plants, HCl contamination can be present in certain feed stocks or can be formed by the hydrolysis of aluminium chloride catalyst.

To minimize aqueous chloride corrosion in the overhead system of crude towers, it is best to keep the salt content of the crude oil charge as low as possible, about 4 ppm. Another way to reduce overhead corrosion would be to inject sodium hydroxide into the crude oil, downstream of the desalter. Up to 10 ppm caustic soda can usually be tolerated.

In most production wells, chloride salts are found either dissolved in water that is emulsified in crude oil or as suspended solids. Salts also originate from brines injected for secondary recovery or from seawater ballast in marine tankers. Typically, the salts in crude oils consist of 75% sodium chloride, 15% magnesium chloride, and 10% calcium chloride. When crude oils are charged to crude distillation units and heated to temperatures above approximately 120 °C, hydrogen chloride is evolved from magnesium and calcium chloride, while sodium chloride is essentially stable up to roughly 750 °C.

Neutralizers are injected into the overhead vapor line of the crude tower to maintain the pH value of the stripping steam condensate between 5 and 6. A pH value above 7 can increase corrosion with sour crudes, as well as fouling and underdeposit corrosion by chloride salt neutralizers.

1.3.1.5 Nitrogen Compounds

Organic nitrogen compounds, such as indole, carbuzole, pyridine, or quinoline, are present in many crude oils, but do not contribute to corrosion problems unless converted to ammonia or hydrogen cyanide. This occurs in catalytic cracking, hydrotreating, and hydrocracking operations, where NH_3HCN, in combination with H_2S and other constituents, becomes the major constituent of sour water, which can be highly corrosive to carbon steel.

Ammonia is also produced in ammonia plants as a raw material for the manufacture of urea and other nitrogen-based fertilizers. Ammonia in synthesis gas at temperatures between 450 and 500 °C causes nitridation of steel components. When synthesis gas is compressed to up to 34.5 MPa (5000 psig) prior to conversion, corrosive ammonium carbonate is formed, requiring various stainless steels for critical components. Condensed ammonia is also corrosive and can cause stress corrosion cracking (SCC) of stressed carbon steel and low-alloy steel components.

1.3.1.6 Sour Water

The term sour water denotes various types of process water containing H_2S, NH_3HCN, and small amounts of phenols, mercaptanes, chlorides, and fluorides. High concentrations of ammonia can saturate process water with ammonium bisulfide (NH_4HS) and causes serious corrosion of carbon steel components. Ammonium bisulfide will also rapidly attack admiralty metal (C44300) tubes. Only titanium Grade 2 (R50400) tubes have sufficient resistance to be used in this case.

1.3.1.7 Polythionic Acids

Combustion of H_2S in refinery flares can produce polythionic acids of the type $H_2S_xO_y$ (including sulfurous acid) and can cause severe intergranular corrosion of flare tips made of stainless steels and high-nickel alloys. Corrosion can be minimized by using lower-nickel alloys such as alloy 825 (N08825) or alloy 625 (N06625). Polythionic acids also cause SCC during shut-down.

1.3.2 Low-Temperature Corrosion by Process Chemicals

Severe corrosion problems can be caused by process chemicals, such as various alkylation catalysts and by-products, organic acid solvents used in certain petrochemical processes, hydrogen chloride stripped off reformer catalysts, and caustic and other neutralizers that ironically, are added to control acid corrosion. A filming-amine corrosion inhibitor can be quite corrosive if injected undiluted (neat) into a hot vapor stream. Another group of process chemicals that are corrosive, or become corrosive, is solvents used in treating and gas-scrubbing operations. These chemicals are as follows:

- Acetic acid
- Aluminum chloride
- Organic chloride
- Hydrogen fluoride
- Sulfuric acid
- Caustic
- Amine
- Phenol.

1.3.2.1 Acetic Acid

Corrosion by acetic acid can be a problem in petrochemical process units for the manufacture of certain organic intermediates such as terephthalic acid. Various types of austenitic stainless steels are used, as well as alloy C-4 (N06455), alloy C-276 (N10276) and titanium, to control corrosion by acetic acid in the presence of small amount of hydrogen bromide or hydrogen chloride.

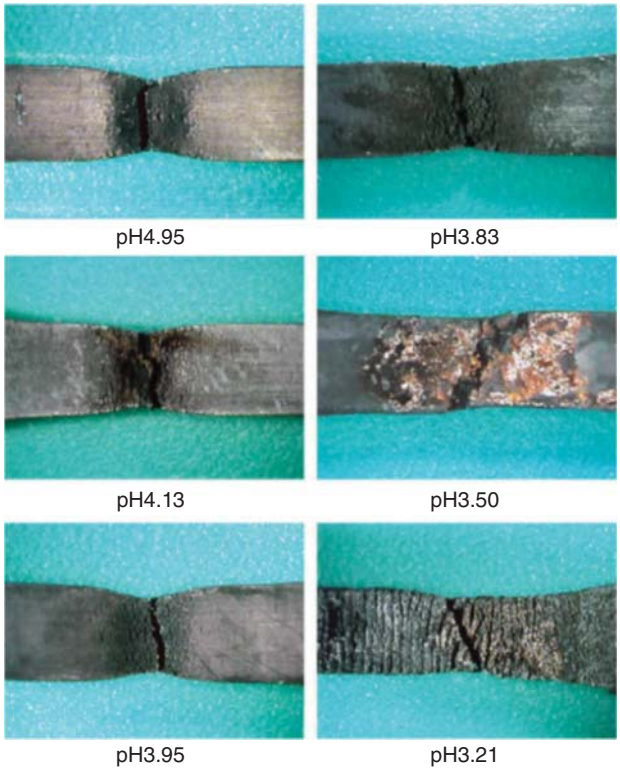


Figure 1.1 *Fracture morphologies (side view) of the 3.5NiCrMoV steels tested at various acetic acid concentrations (pH 3.21–4.95) with a strain rate of $1 \times 10^{-7} s^{-1}$ at 150 °C. (Reprinted from W.Y. Maeng, D.D. Macdonald, 2008, with permission from Elsevier.)*

A small amount of water in the acetic acid can have a significant influence on corrosion. Type 304 (S30400) stainless steel has sufficient resistance to lower concentrations of acetic acid up to the boiling point. Higher concentrations can be handled by type 304 stainless steel if the temperature is below 90 °C.

Corrosion by acetic acid increases with temperature. Bromide and chloride contamination causes pitting and SCC, while addition of oxidizing agents, including air, can reduce corrosion rates by several orders of magnitude. Figure 1.1 shows fracture morphologies (side view) of the 3.5NiCrMoV steels tested at various acetic acid concentrations (pH 3.21–4.95) with a strain rate of $1 \times 10^{-7} s^{-1}$ at 150 °C.

1.3.2.2 Aluminium Chloride

Certain refining and petrochemical processes, such as butane isomerization, ethylbenzene production and polybutene production, use aluminium chloride as a catalyst. It is not corrosive if it is kept absolutely dry, otherwise it hydrolyzes to hydrochloric acid.

During shut-down, equipment should be opened for the shortest possible time. Upon closing, the system should be dried with hot air, followed by inert gas blanketing. Equipment that is exposed to hydrochloric acid may require extensive lining with nickel alloys, such as alloys 400 (N04400), B-2 (N10665), G4 (N06455), or C-276 (N10276).

1.3.2.3 Organic Chloride

Organic chloride in crude oils will form various amounts of hydrogen chloride at the elevated temperatures of crude preheat furnaces. Many crude oils contain small amounts of organic chlorides (5 to 50 ppm), but the major problem is contamination with chlorinated organic solvents during production.

If contaminated crude oil must be run off for distillation, the usual approach is to blend it slowly into uncontaminated crude oil.

1.3.2.4 Hydrogen Fluoride

Some alkylation processes use concentrated HF instead of H_2SO_4 as the catalyst. In general, HF is less corrosive than HCl because it passivates most metals by the formation of protective fluoride films. If these films are destroyed by dilute acid, severe corrosion occurs. Therefore, as long as feedstocks are dry, carbon steel – with various corrosion allowances – can be used for the vessels, piping, and valve bodies of hydrofluoric acid alkylation units. All carbon steel welds that will contact HF, should be post-weld heat treated.

Fractionation towers should have Type 410 (S41000) stainless steel tray valves and bolting, and for desiobutanizer tower tray valves and bolting, alloy 400 (N04400) is recommended. Corrosion problems in HF alkylation units occur after shut-down because pockets of water have been left in the equipment. It is very important that equipment be thoroughly dried by draining all low spots and by circulating hydrocarbon before the introduction of HF catalyst at start-up.

1.3.2.5 Sulfuric Acid

Certain alkylation units use essentially concentrated sulfuric acid as the catalyst; some of this acid is entrained in reactor effluent and must be removed by neutralization with caustic and scrubbing with water. Acid removal may not be complete, however, and traces of acid – at various concentrations (in terms of water) – remain in the stream.

Dilute sulfuric acid can be highly corrosive to carbon steel, which is the principal material of construction for sulfuric acid alkylation units. Because the boiling point of sulfuric acid ranges from 165 to 315 °C, depending on concentration, entrained acid usually ends up in the bottom of the first fractionation tower and reboiler following the reactor; this is where the entrained acid becomes concentrated.

Acid concentrations above 85% by weight are not corrosive to carbon steel if temperatures are below 40 °C. Cold-worked metal (usually used for bends) should be stress relieved. Under ideal operating conditions, few, if any, corrosion and fouling problems occur.

Carbon steel depends on a film of iron sulfate for corrosion resistance, and if this film is destroyed by high velocities and flow turbulence, corrosion can be quite severe.

Figure 1.2 shows corrosion rate as a function of H_2SO_4 concentration for carbon steel with different amounts of carbon. Test temperature: 25 ± 2 °C. Figure 1.3 illustrates a carbon steel ring in 96% reagent-grade H_2SO_4 under static conditions at 25 °C.

1.3.2.6 Caustic

Sodium hydroxide is widely used in refinery and petrochemical plant operations to neutralize acid constituents. At ambient temperature and under dry conditions, NaOH can be handled in carbon steel equipment. Carbon steel is also satisfactory for aqueous caustic solutions below 50–80 °C, depending on concentration. For caustic service above these temperatures, but below 95 °C, carbon steel can also be used if it has been post-weld heat treated to avoid SCC at welds. Austenitic stainless steels, such

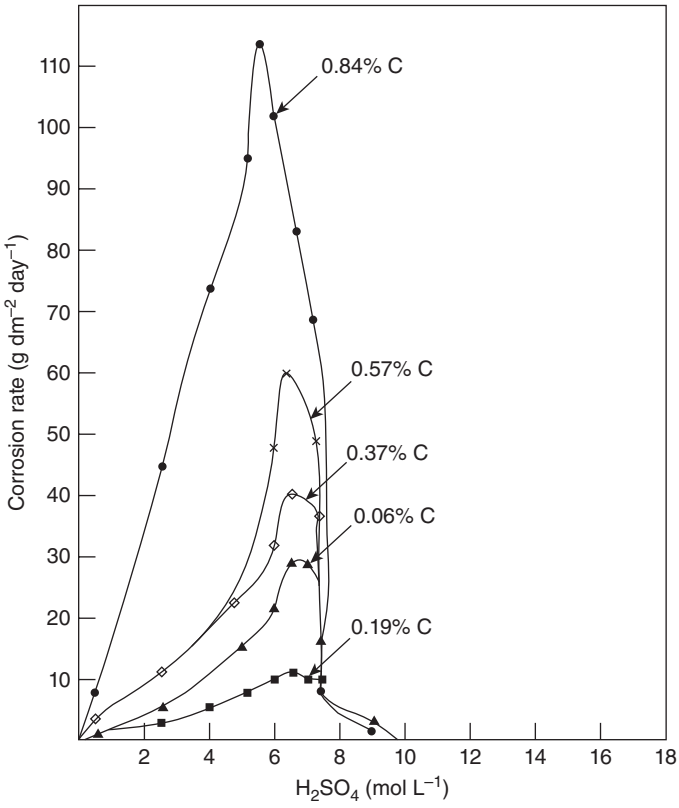


Figure 1.2 *Corrosion rate as a function of H_2SO_4 concentration for carbon steel with different amounts of carbon. Test temperature: 25 ± 2 °C. Test duration: 24 h (except for tests in which the corrosion rate was so high that the steel specimen would have completely corroded). (Reprinted from Z. Panossian* et al.*, 2012, with permission from Elsevier.)*

as Type 304 (S 30400), can be used up to approximately 120 °C, while nickel alloys are required at higher temperatures.

Injecting 3%, instead of 40% NaOH solution minimizes the problem of soda corrosion of the crude transfer line. If caustic is injected too close to an elbow of the transfer line, impingement by droplets of caustic can cause severe attack and a hole-through at the elbow.

1.3.2.7 Amines

Corrosion of carbon steel by amines in gas treating and sulfur recovery units can usually be traced to faulty plant design, poor operating practices, and solution contamination. In general, corrosion is most severe in systems removing only CO_2 and is least severe in systems removing only H_2S.

Systems handling mixtures of the two fall between these two extremes if the gases contain at least 1 vol.% H_2S. Corrosion in amine plants using monoethanolamine is more severe than in those using diethanolamine, because the former is more prone to degradation. Corrosion is not caused by the amine itself, but is caused by dissolved hydrogen sulfide or carbon dioxide and by amine degradation products.

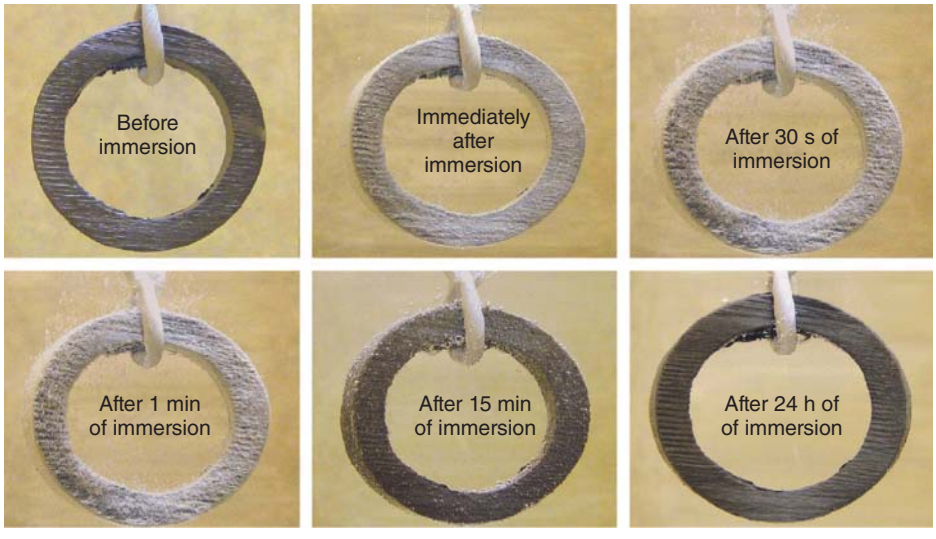


Figure 1.3 *A carbon steel ring in 96% reagent-grade H_2SO_4 under static conditions at 25 °C (Reprinted from Z. Panossian* et al.*, 2012, with permission from Elsevier.)*

1.3.2.8 Phenol

Phenol (carbolic acid) is used in refineries to convert heavy, waxy distillates obtained from crude oil distillation into lubricating oils. As a rule, all components in the treating and raffinate recovery sections, except tubes in water-cooled heat exchangers, are made from carbon steel. If water is not present, few significant corrosion problems can be expected to occur in these sections.

In the extract recovery section severe corrosion can occur, especially where high flow turbulence is encountered. As a result, certain components require selective alloying with Type 316 (S31600) stainless steel. Typically, stainless steel liners are required for the top of the dryer tower, the entire phenol flash tower, and various condenser shells and separator drums that handle phenolic water.

Tubes and headers in the extract furnace should also be made of Type 316 (S31600) stainless steel with U-bends sleeved in alloy C-4 (N06455) on the outlet side to minimize velocity accelerated corrosion.

1.4 High-Temperature Corrosion

Equipment failures can have serious consequences because processes at high temperatures usually involve high pressures as well. With hydrocarbon streams, there is always the danger of fire when ruptures occur.

High-temperature refinery corrosion is caused by various sulfur compounds originating from crude oil. Sulfidic corrosion rate correlations are available and therefore equipment life can be predicted with some degree of reliability. Different types of high-temperature corrosion are named as follows:

- Sulfidic corrosion
- Sulfidic corrosion without hydrogen present
- Sulfudic corrosion with hydrogen present
- Naphthenic acids
- Fuel ash
- Oxidation.

1.4.1 Sulfidic Corrosion

Corrosion by various sulfur compounds at temperatures between 260 and 540 °C is a common problem in many petroleum-refining processes, and occasionally in petrochemical processes. Sulfur compounds originate from crude oils and include polysulfides, hydrogen sulfide, mercaptans, aliphatic sulfides, disulfides, and thiophenes.

With the exception of thiophenes, sulfur compounds react with metal surfaces at elevated temperatures, forming metal sulfide, certain organic molecules, and hydrogen sulfide. Corrosion is in the form of uniform thining, localized attack, or erosion corrosion.

Nickel and nickel-rich alloys are rapidly attacked by sulfur compounds at elevated temperatures, while chromium-containing steels provide excellent corrosion resistance (as does aluminium). Combinations of hydrogen sulfide and hydrogen can be particularly corrosive, and as a rule, austenitic stainless steels are required for effective corrosion control.

1.4.2 Sulfidic Corrosion without Hydrogen Present

This type of corrosion occurs in various components of crude distillation, catalytic cracking, hydrotreating, and hydrocracking units upstream of the hydrogen injection line.

Preheat-exchanger tubes, furnace tubes, and transfer lines are generally made from carbon steel, as is the corresponding equipment in the vacuum distillation section. The lower shell of distillation towers, where temperatures are above 230 °C is usually lined with stainless steel containing 12% Cr, such as Type 405. Trays are made of stainless steel containing 12% Cr. Even with the low corrosion rates of carbon steel, certain tray compounds, such as tray valves, may fail in a short time because attack occurs from both sides of a relatively thin piece of metal.

Metal skin temperature, rather than flow stream temperatures, should be used to predict corrosion rates when significant differences between the two arise. For example, metal temperatures of furnace tubes are typically 85 to 110 °C higher than the temperature of the hydrocarbon stream passing through the tubes. Furnace tubes normally corrode at a higher rate on the hot side (fire side) than on the cool side (wall side).

1.4.3 Sulfidic Corrosion with Hydrogen Present

The presence of hydrogen in, for example, hydrotreating and hydrocracking operations, increases the severity of high-temperature sulfidic corrosion. Hydrogen coverts organic sulfur compounds in feed stocks to hydrogen sulfide; corrosion becomes a function of H_2S concentration.

Downstream of the hydrogen injection line, low-alloy steel piping usually requires aluminizing in order to minimize sulfidic corrosion. Alternatively Type 321 (S32100) stainless steel can be used. Tubes in the preheat furnace are aluminized low-alloy steel, or aluminized 12% Cr stainless steel. Reactors are usually made of 2.25 Cr-1 Mo steel, either with a Type 347 (S34700) stainless steel weld overlay or an internal factory lining. Reactor internals are often Type 321 stainless steel.

When selecting materials for this service, the recommendations of API 941-2004 should be followed to avoid problems with high-temperature hydrogen attack.

The most practical corrosion rate correlations seem to be the so-called Cooper–Gorman curves based on a survey conducted by the NACE Committee T-8 on Refining Industry Corrosion. A modified Cooper–Gorman curve is shown in Figure 1.4. To facilitate use of these curves the original segments of the curves have been extended (dashed lines).

Stainless steels containing at least 18% Cr are often required for complete immunity to corrosion because Cooper–Gorman curves are primarily based on corrosion rate data for an all-vapor system; partial condensation can be expected to increase corrosion rates because of droplet impingement.

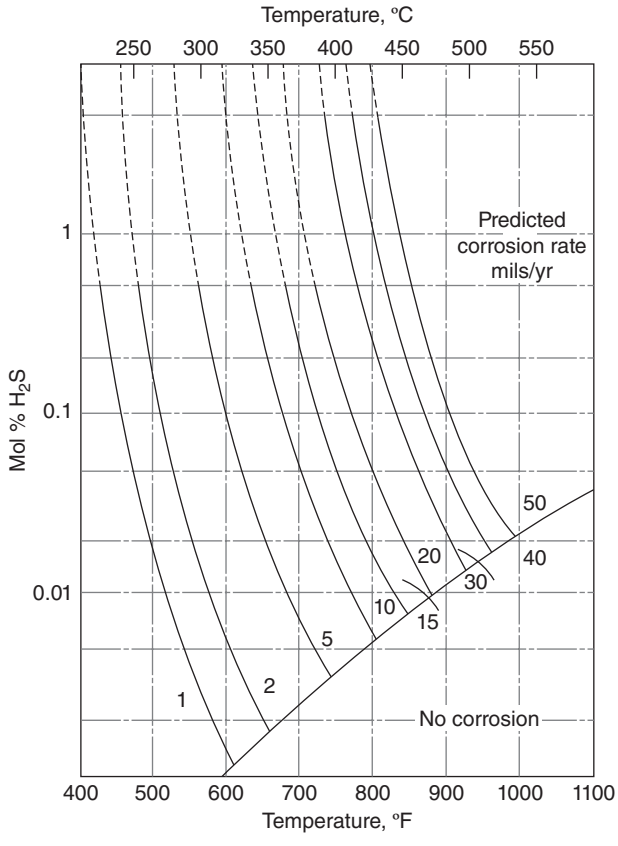


Figure 1.4 *Effect of temperature and hydrogen sulfide content on high-temperature H_2S/H_2 corrosion of 5 Cr-0.5 Mo steel (naphtha desulfurizers) 1 mil/yr = 0.025 mm/yr. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers. www.wescef.com.au)*

1.4.4 Naphthenic Acids

These organic acids are present in many crude oils. The general formula may be written as $R(CH_2)_nCOOH$, where R is usually a cyclopentane ring. The higher molecular weight acids can be bicyclic ($12 < n > 20$), tricyclic ($n > 20$), and even polycyclic. Naphthenic acid content is generally expressed in terms of the neutralization number (total acid number), which should be evaluated by ASTM D 664 as mg KOH/grams of sample.

This acid is corrosive only at temperatures above 230 °C in the neutralization number range of 1 to 6 encountered with crude oil and various side-cuts. At any given temperature, the corrosion rate is proportional to the neutralization number, and triples with each 55 °C increase in temperature.

In contrast to high-temperature sulfidic corrosion, no protective scale is formed, and low-alloy and stainless steels containing up to 12% Cr provide no benefits whatsoever over carbon steel. The presence of naphthenic acids may accelerate high-temperature sulfidic corrosion that occurs at furnace headers, elbows, and tees of crude distillation units because of unfavorable flow conditions.

Severe naphthenic acid corrosion (in the form of pitting) has been experienced in the vacuum towers of crude distillation units in the temperature zone of 290 to 345 °C and sometimes as low as 230 °C. Attack is often limited to the inside and the very top of the outside surfaces of bubble caps. Figure 1.5

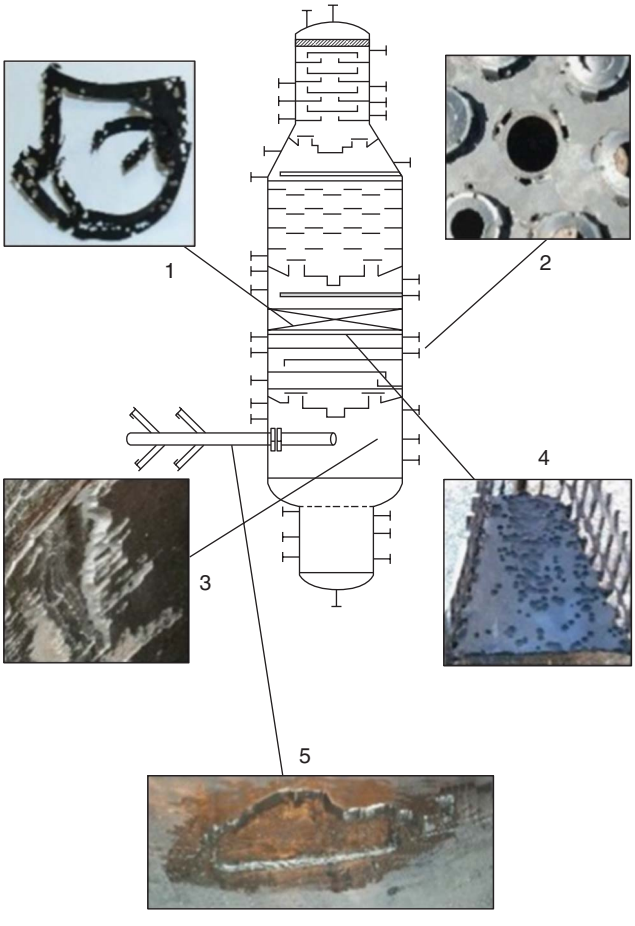


Figure 1.5 *Different kinds of corrosion morphologies associated with naphthenic acid attack. Region 1 is the IMPT random packing, region 2 is the tray and bubble caps, region 3 is the column wall flash zone, region 4 is the support grid, and region 5 is the transfer line. (Reprinted from P.P. Alvisi, V.F.C. Lins, 2011, with permission from Elsevier.)*

shows different kinds of corrosion morphologies associated with naphthenic acid attack. Region 1 is the IMPT random packing, region 2 is the tray and bubble caps, region 3 is the column wall flash zone, region 4 is the support grid, and region 5 is the transfer line.

Attacks on bubble caps are due to impinging droplets of condensing acids. Naphthenic acid corrosion is most easily controlled by blending crude oils having high neutralization numbers with other crude oils, in order to keep this neutralization number between 0.5 and 1.0. However, this does not prevent corrosion of vacuum tower internals operating in the 290 to 345 °C range. These should be made from Type 316 (S31600) or, preferably, Type 317 (S31700) stainless steel containing at least 3.5% Mo. The vacuum tower lining in this temperature range should also be Type 317 (S31700) stainless steel. Aluminum has excellent resistance to naphthenic acid corrosion in vacuum towers and can be used if its strength limitations and low resistance to velocity effects are kept in mind. Alloy 20 (N08020) and titanium Grade 2 (R50400) are also resistant to naphthenic acid corrosion. In contrast, aluminized carbon steel tray components, such as bubble caps, have performed poorly.

1.4.5 Fuel Ash

Corrosion by fuel ash deposits can be one of the most serious operating problems with boiler and preheat furnaces. All fuels except natural gas contain certain inorganic contaminants that leave the furnace with products of combustion. These will deposit on heat-receiving surfaces, such as superheater tubes, and after melting can cause severe liquid-phase corrosion.

Contaminants of this type include various combinations of vanadium, sulfur, and sodium compounds. Fuel ash corrosion is most likely to occur when residual fuel oil (Bunker C fuel) is burned. In particular, vanadium pentoxide vapor (V_2O_5) reacts with sodium sulfate (Na_2SO_4) to form sodium vanadate ($Na_2O.6V_2O_5$). The latter compound reacts with steel, forming a molten slag that runs off and exposes fresh metal to attack. Corrosion increases sharply with increasing temperature and the vanadium content of the fuel oil. If the vanadium content exceeds 150 ppm, the maximum tube wall temperature should be limited to 650 °C. Between 20 and 150 ppm V, the maximum tube wall temperature can be between 650 and 845 °C, depending on the sulfur content and the sodium–vanadium ratio of the fuel oil. With 5 to 20 ppm V, the maximum tube wall temperature can exceed 845 °C.

In general, most alloys are likely to suffer from fuel ash corrosion. However, alloys with high chromium and nickel contents provide the best resistance to this type of attack. Sodium vanadate corrosion can be reduced by firing boilers with low excess air (< 1%). This minimizes the formation of sulfur trioxide in the firebox and produces high-melting slags containing vanadium tetroxide and trioxide rather than pentoxide. In the temperature range 400 to 480 °C, boiler tubes are corroded by alkali pyrosulfates such as sodium pyrosulfate and potassium pyrosulfate, when appreciable concentrations of sulfur trioxide are present.

Additives can be helpful in controlling corrosion, particularly in conjunction with firing in low excess air. The effectiveness of the additives varies. The most useful additives are based on organic magnesium compounds.

Additives raise the melting point of fuel ash deposits and prevent the formation of sticky and highly corrosive films. Instead, a porous and fluffy deposit layer is formed with additives that can be readily removed by periodic cleaning. Magnesium-type additives offer additional benefits with regard to cold-end corrosion in boilers. Sulfuric acid condenses at temperatures between 150 and 175 °C (300 and 350 °F), depending on the sulfur content of the fuel oil, and can cause serious corrosion problems. Additives neutralize any free acid by forming magnesium sulfate.

1.4.6 Oxidation

Carbon steels, low-alloy steels and stainless steels react at elevated temperatures with oxygen in the surrounding air and become scaled. Nickel alloys can also become oxidized, especially if spalling of scale occurs. The oxidation of copper alloys usually is not a problem, because these are rarely used where operating temperatures exceed 260 °C.

Alloying with both chromium and nickel increases scaling resistance. Stainless steels or nickel alloys, except alloy 400 (N04400), are required to provide satisfactory oxidation resistance at temperatures above 705 °C. Thermal cycling, applied stresses, moisture and sulfur-bearing gases will decrease scaling resistance.

High-temperature oxidation is limited to the outside surfaces of furnace tubes, tube hangers and other parts that are exposed to combustion gases containing excess air.

At elevated temperatures, steam decomposes at metal surfaces to hydrogen and oxygen, and may cause steam oxidation, which is more severe than air oxidation at the same temperature. Fluctuating steam temperatures tend to increase the rate of oxidation by causing scale to spall and thus expose fresh metal to further attack.

2

Corrosion Problems in the Petroleum and Chemical Industries

This chapter reviews some representative types of corrosion problems encountered in the various facets of the petroleum and chemical industries. The fundamental processes underlying these corrosion problems are examined. In addition, commonly used methods for corrosion prevention and control are discussed

2.1 Stress Corrosion Cracking and Embrittlement

Stress corrosion cracking (SCC) is the growth of cracks in a corrosive environment. It can lead to unexpected sudden failure of normally ductile metals subjected to a tensile stress, especially at elevated temperatures. SCC is highly chemically specific in that certain alloys are likely to undergo cracking only when exposed to a small number of chemical environments.

The chemical environment that causes stress corrosion cracking for a given alloy is often one that is otherwise only mildly corrosive to that metal. Hence, metal parts with severe SCC can appear bright and shiny, while being filled with microscopic cracks. This factor makes it common for stress corrosion cracking to go undetected prior to failure.

Stress corrosion cracking often progresses rapidly, and is more common among alloys than pure metals. The specific environment is of crucial importance, and only very small concentrations of certain highly active chemicals are needed to produce catastrophic cracking, often leading to devastating and unexpected failure.

SCC and environmental embrittlement are the most insidious forms of failure that can be experienced by process equipment, because they tend to strike without warning. There is no noticeable yielding or bulging of the component, there is no measurable metal loss, and through-thickness cracks can form in as little as 1 to 2 h after initial exposure to a crack-inducing environment. For example, cracking throughout an entire furnace coil occurred within 1 h after exposure to air and the resultant formation of polythionic acids.

Figure 2.1 shows typical stress corrosion cracking in heat exchanger tube.

Corrosion and Materials Selection: A Guide for the Chemical and Petroleum Industries, First Edition. Alireza Bahadori.
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Figure 2.1 *Typical stress corrosion cracking in a heat exchanger tube. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers. www.wescef.com.au.)*

Towers and heat exchangers have had to be scrapped because of hydrogen blistering, embrittlement, and stress cracking at welds. High-temperature hydrogen attack has resulted in the sudden rupture of pressure vessels. Environments effecting stress-corrosion cracking are summarized as follows:

- Chlorides
- Caustics
- Ammonia
- Amines
- Polythionic acids.

2.1.1 Chloride Cracking

Chlorides are the most common cause of SCC in austenitic stainless steels and nickel alloys. In theory, one would need a single chloride ion in water, with sufficient oxygen and residual stresses present, to cause cracking. In practice, however, the permissible limits on chloride ion content are higher.

The usual failure mode of chloride SCC in austenitic stainless steels is transgranular, highly branched cracking. Intergranular cracking is sometimes associated with transgranular cracking, but this is not common. If it occurs, it is usually because of a sensitized micro-structure.

Based on laboratory tests in boiling 42% magnesium chloride solution, austenitic stainless steel and nickel alloys are subject to chloride SCC if their nickel content is less than about 45%. The heat treatment of an alloy was found to have no effect on its resistance to chloride SCC. In practice, however, stainless steel and nickel alloys containing greater than 30% Ni will be immune in most refinery environments. Figure 2.2 shows typical chloride-induced SCC.



Figure 2.2 *Chloride-induced stress corrosion cracking. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers. www.wescef.com.au.)*

Factors that influence the rate and severity of cracking are chloride content, oxygen content, temperature, stress level, and pH value of an aqueous solution. It has been established that oxygen is required for chloride cracking to occur. Refinery and petrochemical plant experience confirms that stainless steel components, such as heat-exchanger tube bundles, usually do not crack until removed from operation and exposed to air during a shut-down. Increased oxygen content decreases the critical chloride content for cracking to occur. Figure 2.3 shows the synergistic effect of chlorides and oxygen on the SCC of Type 304 stainless steel.

The severity of cracking increases with temperature. Cracking of austenitic stainless steel components rarely occurs at ambient temperatures. Stainless steel pump impellers in seawater service have shown no cracking problems, despite the fact that both chloride and oxygen contents are high.

Cracking has been found to occur, however, at tropical locations where exposure to direct sunlight can increase metal temperatures significantly above ambient. As a general rule, chloride SCC of process equipment occurs only at temperatures above about 65 °C (145 °F).

The stresses required to produce cracking can be assumed to be always present. Residual stresses from forming, bending, or joining operations are sufficient for cracks to form. Thermal stress-relief treatments at 870 °C (1600 °F) can effectively prevent cracking if done correctly and without the necessity for subsequent cold working (to correct distortion, for example).

In alkaline solutions, the likelihood of chloride SCC is greatly reduced. Consequently, austenitic stainless steels are frequently used for equipment exposed to amine solutions in gas treatment and sulfur recovery units.

Most cracking problems occur when unexpected chloride concentrations are found in process streams or in the atmospheric environment. For example, chloride SCC was caused by seawater spray carried by prevailing winds. The spray soaked the insulation over Type 304 stainless steel, chlorides were concentrated by evaporation, and cracking occurred at areas with residual weld stresses. Other frequent causes of cracking are water dripping on a warm pipe and water leaching chlorides from insulation.

As discussed previously, chlorides are present in a number of refining units, including crude distillation, hydrocracking, hydrotreating, and reforming. Chlorides are also found in other units as contamination from upstream processing, or they are introduced with the stripping stream, process water, or cooling water.

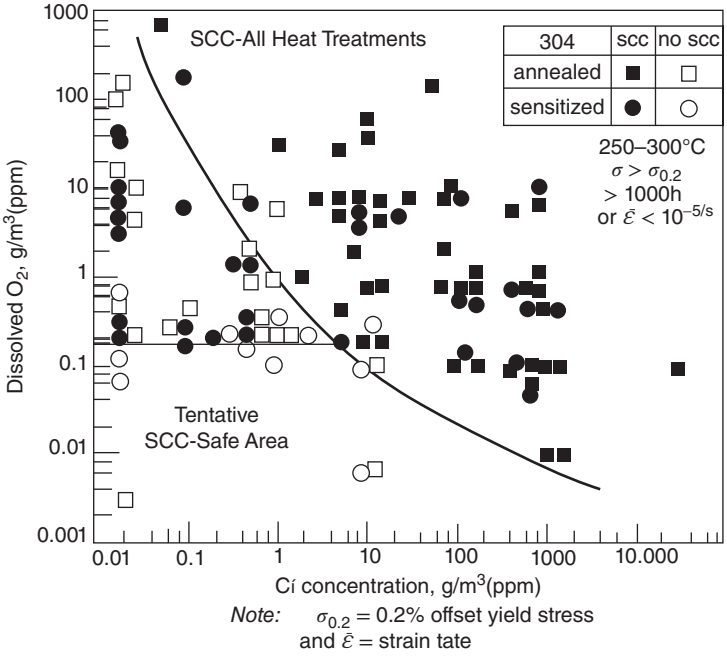


Figure 2.3 *Synergistic effect of chlorides and oxygen on the stress corrosion cracking of Type 304 (S30400) stainless steel. The tests were conducted at 250 to 300°C (480 TO 570°F). (Reproduced with permission from Daubert Cromwell.)*

The latter is a particular problem in petrochemical processes that use stainless steel heat exchangers to make steam as a means of recovering waste heat. Any chloride contamination of boiler feedwater can result in chlorides concentrating in heat-exchanger tubes and can cause pitting and SCC. As a rule, austenitic stainless steels are not recommended for components in which water is likely to evaporate or condense out.

When good resistance to aqueous sulfide corrosion is required, ferritic stainless steels or duplex stainless steels can be substituted for austenitic stainless steel. Ferritic stainless steels, such as Type 405 (S40500) or Type 430 (S43000), are not susceptible to chloride SCC. The duplex stainless steels have a mixed ferritic–austenitic structure and are resistant to chloride SCC, but not to highly aggressive chloride environments.

For example, cold-worked Type 329 (S32900) stainless steel has cracked when chlorides were concentrated by vaporization of a process stream. Some of the new proprietary duplex stainless steels, such as 3RE60 (S31500) and 2205 (S31803), have reportedly shown increased resistance toward chloride SCC.

There are no simple methods for preventing SCC when an austenitic stainless steel must be used in an environment known to contain chlorides. Chloride SCC in refineries and petrochemical plants often occurs under shut-down conditions when air and moisture enters equipment opened for inspection and repair. It has been found that the precautionary measures outlined in NACE RP-01-70 for the prevention of cracking by polythionic acids also help prevent cracking by chlorides.

In particular, excluding air and moisture by nitrogen blanketing and rinsing equipment with an aqueous 0.5% sodium nitrate or sodium carbonate 3–5% solution have been shown to inhibit chloride SCC. To prevent cracking on the outside of insulated pipe, aluminum foil has been wrapped between the insulation and pipe to provide some measure of cathodic protection.

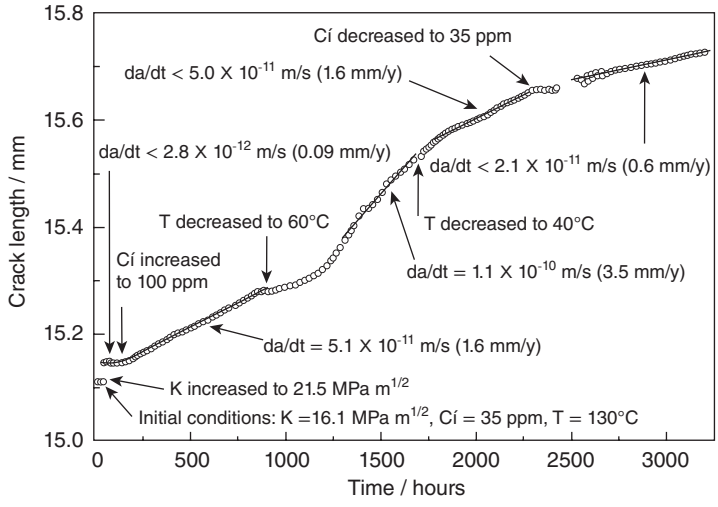


Figure 2.4 *Stress corrosion crack growth of 321 stainless steel in response to chloride and temperature excursion. The initial and the final stress intensity factors are 16.1 MPa m$^{1/2}$ and 22.3 MPa m$^{1/2}$, respectively. (Reprinted from A. Turnbull, S. Zhou, 2008, with permission from Elsevier.)*

One method of preventing the catastrophic failure of components by chloride SCC would be the use of austenitic stainless steel as an internal cladding. The highly branched mode of any cracking would effectively prevent the development of stress raisers. Carbon or low alloy steel base metal would not be susceptible to cracking in chloride solutions, but some localized corrosion may occur. This type of construction would also provide resistance to cracking when chlorides are liable to contact the outside of the components, as in external insulation, for example.

Figure 2.4 shows stress corrosion crack growth of a 321 SS in response to chloride and temperature excursions, the initial and the final stress intensity factors are 16.1 MPa m$^{1/2}$ and 22.3 MPa m$^{1/2}$, respectively. Figure 2.5 illustrates SCC in a 316 stainless steel chemical processing piping system.

2.1.2 Caustic Cracking

Stress corrosion cracking of various steels and stainless steels by caustic (sodium hydroxide) is also fairly common in refinery and petrochemical plant operations. Cracking is promoted by small amounts of dissolved oxygen.

Sodium chloride, lead oxide, silica, silicates, sulfates, nitrates, permanganates, and chromates cause the active potential to move slightly in the positive (noble) direction. Large amounts of these substances act as inhibitors by pushing the corrosion potential into the passivation range. Phosphates, acetates, carbonates, and tannins also act as inhibitors.

Caustic is added in the form of a 5 to 40% aqueous solution to certain process streams in order to neutralize residual acid catalysts, such as sulfuric, hydrofluoric, and hydrochloric acids. Caustic is also added to cooling water and boiler feedwater to counteract large decreases in pH value due to process leaks.

Traces of caustic can become concentrated in boiler feedwater and cause SCC (caustic embrittlement). This occurs in boiler tubes that alternate between wet and dry conditions (steam blanketing) because of overfiring. Locations such as cracked welds or leaky tube rolls can form steam pockets with cyclic overheating and quenching conditions. These frequently lead to caustic embrittlement.



Figure 2.5 *Stress corrosion cracking in a 316 stainless steel chemical processing piping system. (Reproduced with permission from Daubert Cromwell.)*

Caustic SCC of carbon steel occurs at temperatures above 50 to 80 °C (120 to 180 °F), depending on caustic concentration. Welded carbon steel components that are exposed to caustic solutions above these temperatures should be post-weld heat treated at 620 °C (115 °F) for 1 h per 25 mm (1 in.) of metal thickness. Caustic SCC of austenitic stainless steels occurs between 105 and 205 °C (220 and 400 °F), depending on caustic concentration.

Cracking of austenitic stainless steels is often difficult to distinguish from cracking by chlorides, particularly because common grades of caustic also contain some sodium chloride. As a general rule, however, SCC by chlorides is usually, but not always, in the form of transgranular cracking, while caustic causes intergranular cracking, sometimes accompanied by transgranular cracking due to the presence of chlorides.

Caustic SCC of carbon steel is often initiated at discontinuities in areas of surface deformation as a result of coldworking or welding operations.

Although caustic cracking occurs over a wide range of temperatures, these appears to be no correlation between temperature and time to failure. Because few failures have been reported at near-ambient temperatures, it appears that crack initiation times are inordinately long unless precracking, for example, in the form of weld defects, has occurred. Caustic cracking of carbon steel has been found to occur over a narrow range of potentials near the active current peak of potential/log current curves.

Typically, this potential range is centered about −700 mV versus the Standard Hydrogen Electrode (SHE). The most negative (active) potential for inducing caustic cracking coincides with the potential for initiating passivation by magnetite (Fe_3O_4) formation.

2.1.3 Ammonia Cracking

Ammonia has caused two types of SCC in refineries and petrochemical plants. The first is cracking of carbon steel in anhydrous ammonia service, and the second type is cracking of copper alloys, such as admiralty metal (C 44300). In copper alloys, SCC can occur with ammonia-base neutralizers that are added to control corrosion.

Carbon steel storage vessels, primarily spheres, have developed stress corrosion cracks in anhydrous ammonia service at ambient temperature but elevated pressure. In most cases, cracking was detected by inspection before leakage or rupture, but there were at least two catastrophic failures. There have been few problems with semi-refrigerated storage vessels and no documented cases of SCC in cryogenic storage vessels. The primary causes of cracking are high stresses, hard welds, and air contamination.

To minimize the likelihood of cracking, only low-strength steels, with a maximum tensile strength of 483 MPa (70 ksi), should be used in anhydrous ammonia service. Welds should be post-weld heat treated at 595 °C (1100 °F) or higher, with a maximum allowable hardness of 225 HB.

A water content of at least 0.2% should be maintained in the ammonia because water has been found to be an effective inhibitor of cracking. Air contamination increases the tendency toward cracking and should be minimized, if necessary by the addition of hydrazine to the water. With a water content of 10 ppm, the oxygen content should be below 10 ppm for safe operation. The permissible oxygen content increases to 100 ppm with a water content of 0.1 %. Regular inspection of all components in anhydrous ammonia service is recommended.

Cracking of admiralty metal (C 44300) heat-exchanger tubes has been a recurring problem in a number of refining units and petrochemical process units. For example, ammonia is often used to neutralize acidic constituents, such as hydrogen chloride or sulfur dioxide, in overhead systems of crude distillation or alkylation units, respectively. Stripped sour water containing residual ammonia is used as desalter water at some crude distillation units. This practice causes ammonia contamination of the overhead system even if no ammonia is added intentionally.

Ammonia is formed from nitrogen-containing feed stocks during catalytic cracking, hydrotreating, and hydrocracking operations. As a rule, cracking of admiralty metal (C 44300) tubes occurs only during shut-downs when ammonia-containing deposits on the tube surface become exposed to air. To prevent cracking, tube bundles should be sprayed with a very dilute solution of sulfuric acid immediately after they are pulled from their shells in order to neutralize any residual ammonia. Cracking of admiralty metal (C 44300) tubes has occasionally been attributed to traces of ammonia in cooling water.

2.1.3.1 Estimate of the Rate of Ammonia Cracking Growth

It has been suggested that crack growth in ammonia tanks follows the relationship:

$$a = FK^2t^{0.5} \tag{2.1}$$

where:

$a =$ crack depth in mm at time t, years
$F =$ constant, 3×10^{-4} at ambient temperature and 1×10^{-4} at −33 °C
$K =$ stress intensity factor for the crack in MPa.m^{½}

It is suggested that stress intensity values are in the range 30 to 120 MPa.m^{½}.

Without details of crack size, particularly the critical crack size, and stresses involved it is difficult to estimate the crack growth rate more accurately. As the crack develops it will eventually attain a critical size and failure will occur. It is important to note that the subcritical crack growth rate decreases in time and that cracks are generally small.

Where there is a lack of data, a first-order estimate is used to provide a basis for comparison (i.e. risk ranking) and a baseline until inspection data is available. The following assumptions are made:

- Initial stress intensity, 50 MPa.m$^{1/2}$
- Initial defect size, 3 mm at ambient, 1 mm at −33 °C
- The defect geometry and stresses acting on the defect are unaffected as the defect grows
- The critical stress intensity (i.e. limit state) is assumed to 120 MPa.m$^{1/2}$.

The assumption that the defect geometry is unchanged implies that the stress intensity factor can be calculated.

$$K = \sigma\sqrt{2\pi a}.Y \tag{2.2}$$

where:

$\sigma =$ stress causing the stress intensity, K
$a =$ cracklength
$Y =$ geometry and shape factor.

With the assumption of unchanging stress and defect geometry, this can simplified to:

$$K = C\sqrt{a} \tag{2.3}$$

With the initial values given, C is derived for the case discussed:

$$C = \frac{50}{\sqrt{3}} = 28.87$$

and the generalized relation between K and a is given by:

$$K = 28.87\ \sqrt{\mathrm{a}}$$

This is used to calculate the expected defect size at a given time and stress intensity factor. Combining the two equations allows calculation of approximate crack growth rate, i.e the expected crack depth for given values of K and a is calculated by Equation (2.1) for the first year. A new K value (due to the larger defect) is calculated from Equation (1.2) and a new defect size calculated from Equation (2.1). The process is iterated each year until the critical value is reached.

It should be emphasized that this is a coarse approximation and applies to defects above 3 mm in size at ambient and 1 mm at −33°C, both assuming a 50 Mpa.m$^{1/2}$ stress inetnsity (Figures 2.6

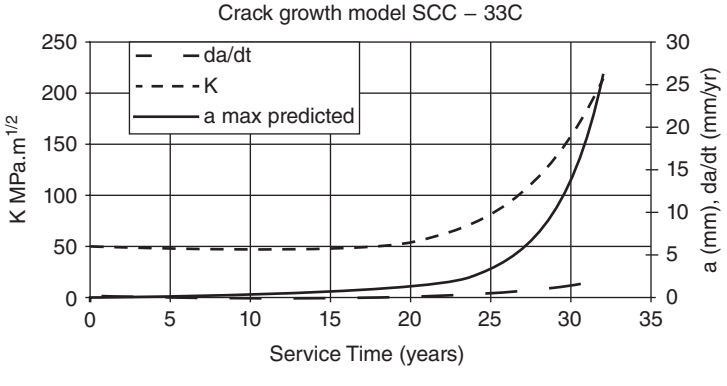


Figure 2.6 *Crack growth: initial 1 mm crack with 50 MPa.m$^{1/2}$ at −33°C. (Reproduced with permission from Daubert Cromwell.)*

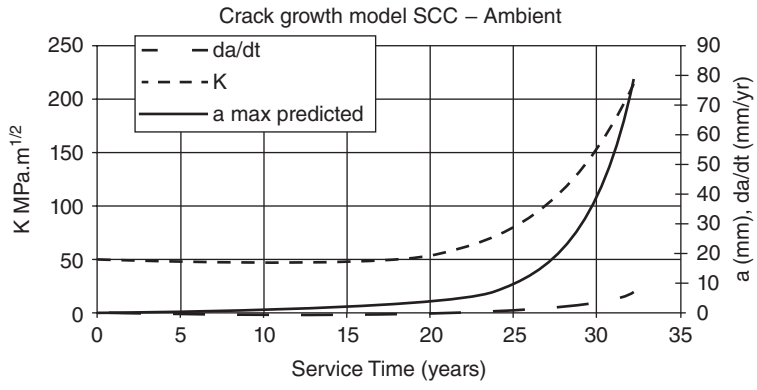


Figure 2.7 *Crack growth: initial 3 mm crack with 50 MPa.m$^{1/2}$ at ambient temperature. (Reproduced with permission from Daubert Cromwell.)*

and 2.7, respectively). The 3 mm defect is obviously more severe. In both cases these assumptions show that service lifetime is around 30 years.

The model could be improved if the input parameters (a and K) were treated as distributions rather than discrete numbers. The results have beecn checked against another example where a 4 mm crack grows to a critical size (15 mm) in 9–10 years and lifetimes over 30 years are expeted at −33°C.

Once inspection data are available, a more rigorous probabilistic approach may be used. If cracks are detected, then a fracture mechanism analysis should be used to detemine the actual stress intensity and the approximate critical crack depth for the actual component.

2.1.4 Amine Cracking

Stress corrosion cracking of carbon steel by aqueous amine solutions, which are used to remove hydrogen sulfide and carbon dioxide from refinery and petrochemical plant streams, has been a recurring problem for number of years.

Cracking was found primarily at temperatures ranging from 50 °C up to 95 °C. Cracking was intergranular, with the crack surface covered by a thin film of magnetite. No cracks were found in piping that had received post-weld heat treatment.

To prevent amine SCC, post-weld heat treatment at 620 °C is recommended for carbon steel welds exposed to amine solutions at temperatures exceeding 95 °C.

2.1.5 Polythionic Acid Cracking

Polythionic acid SCC occurs only in austenitic stainless steels and nickel–chromium–iron alloys that have become sensitized through thermal exposure. Sensitization occurs when the carbon present in the alloy reacts with chromium to produce chromium carbides at the grain boundaries. As a result, the areas adjacent to the grain boundaries become depleted in chromium and are no longer fully resistant to certain corrosive environments.

Sensitization of Type 304 (S30400) stainless steels normally occurs at temperatures between 370 and 815 °C (750 and 1500 °F), whenever the alloy is slowly cooled through this temperature range (such as during welding and heat treating), or during normal process operations. The higher the temperature, the shorter the time of exposure required for sensitization.

Addition of stabilizing elements, such as titanium or niobium, or limiting the amount of carbon are two methods for reducing the effects of welding and heat treating on sensitization. However, they

are not effective for long-term exposure to temperatures above 430 °C (800 °F). The resistance of titanium-stabilized Type 321 (S32100) stainless steel to polythionic SCC can be significantly improved by thermal stabilization at approximately 900 °C (1650 °F), held for 2 h, with no specific limits on the cooling rate.

Laboratory studies and plant experience have demonstrated that austenitic stainless steels are not sensitized when applied as a weld overlay over carbon or low-alloy steels. SCC of the roll-bonded cladding stops at the weld overlay around the nozzle.

Polythionic acids of the type $H_2S_xO_y$ (including sulfurous acid) are formed by the reaction of oxygen and water with the iron/chromium sulfide scale that covers the surfaces of austenitic stainless steel components as a result of high-temperature sulfidic corrosion. Because neither oxygen nor water is present during normal operation under conditions in which austenitic stainless steels would be used, SCC evidently occurs during shut-downs. Oxygen and water originate from steam or wash water used to free components of hydrocarbons during shut-down before inspection, or simply from atmospheric exposure. In catalytic cracking units, oxygen and water can be present during normal operations at certain locations of the catalyst regeneration system because of steam purges and water sprays for preventing catalyst accumulation. The components involved include air rings, plenums, slide valves, cyclone components, and expansion joint bellows in the catalyst regenerator and associated lines.

In general, however, SCC by polythionic acids is considered to be a problem primarily during shut-down periods; suitable procedures to prevent cracking are outlined in NACE RP-01-70. These procedures include nitrogen purging of components that have been opened to the atmosphere, purging with dry air having a dew point below −15 °C (5 °F), or neutralizing any polythionic acids that are formed by washing components with a 2% aqueous soda ash (sodium carbonate) solution. Soda ash solution should also be used for hydrotesting prior to returning components to service.

2.1.6 Hydrogen Damage

Corrosion of carbon and low-alloy steels by aqueous hydrogen sulfide solutions or sour water can result in one or more types of hydrogen damage. These include loss of ductility on slow application of strain (hydrogen embrittlement), formation of blisters or internal voids (hydrogen blistering), and spontaneous cracking of high-strength or high-hardness steels (hydrogen stress cracking).

Hydrogen stress cracking of embrittled metal is caused by static external stresses, transformation stresses (for example, as a result of welding), internal stresses, cold working, and hardening. As a rule, cracking does not occur in ductile steels or in steels that have received a proper post-weld heat treatment.

Hydrogen damage occurs primarily when steel is exposed to aqueous hydrogen sulfide solutions having low pH values. Aqueous hydrogen sulfide solutions with high pH values can also cause hydrogen damage if cyanides are present. In the absence of cyanides, aqueous hydrogen sulfide solutions with pH values above 8 do not corrode steel, because a protective iron sulfide film forms on the surface.

Cyanides destroy this protective film and convert it into soluble ferrocyanide [$Fe(CN)_6^{-4}$] complexes. As a result, the now unprotected steel can corrode very rapidly. For practical purposes, the corrosion rate depends primarily on the disulfide ion (SH^-) concentration and, to a lesser extent, on the cyanide ion (CN^-) concentration. The more disulfide ion is present, the more cyanide is required to destroy the protective iron sulfide film. It has been shown experimentally that corrosion of steel in aqueous ammonia/sulfide/cyanide solutions with pH values above 8 is always accompanied by hydrogen damage. Hydrogen damage has different types, as follows:

- Hydrogen embrittlement
- Hydrogen blistering
- Hydrogen stress cracking.

2.1.6.1 Hydrogen Embrittlement

Hydrogen embrittlement is a well-known phenomenon in the degradation of mechanical properties of steels in the presence of hydrogen. An important result of hydrogen embrittlement (hereafter referred to as HE) is premature failure of structural metals in pipeline steels and hydrogen transport cylinders. In the near future, as economies begin to utilize hydrogen as an energy source, specific applications such as fuel cells for vehicles will require storage at very high hydrogen pressures in order to provide ranges competitive with the current gas-powered vehicles. Because of the volatility of the gas, failure of storage vessels poses a significant risk, and a feasible solution must be developed in order to ensure the safety of the public.

Hydrogen embrittlement is characterized by decreasing ductility with decreasing strain rate; this is contrary to metal behavior in most other types of embrittlement. For example, the ductility of carbon steel has been reported to drop from 42 to 7%, when charged with hydrogen.

This loss of ductility is only observed during slow strain rate testing and conventional tensile tests, but not during impact tests, such as the Charpy V-notch test. Failure, in the form of cracking, usually occurs sometime after a load is applied to hydrogen-charged steel. Because this phenomenon is also known as static fatigue, the minimum load for failure to occur is known as the static fatigue limit.

Hydrogen embrittlement is temporary and can be reversed by heating the steel to drive out the hydrogen. The rate of recovery depends on time and temperature. Heating to 230 °C (450 °F) and holding for 1 h per 25 mm (1 in.) of thickness has been found to be adequate to prevent cracking after welding.

Although temperatures as high as 650 °C (1200 °F) for 2 h or as low as 105 °C (225 °F) for 1 day have reportedly been used to restore full ductility, even the heat of the sun on a summer day was found to be sufficient to restore ductility to a high-carbon cold-drawn steel wire that had been embrittled by exposure to wet hydrogen sulfide. As a rule, however, heating to temperatures above 315 °C (600 °F) for any length of time should be avoided to lessen the possibility of high-temperature hydrogen attack.

Titanium can also become embrittled by absorbed hydrogen as a result of corrosion or exposure to dry hydrogen gas. When hydrogen is absorbed by titanium in excess of about 150 ppm, a brittle titanium hydride phase will precipitate out. This type of embrittlement is usually permanent and can be reversed only by vacuum annealing, which is difficult to perform.

Absorption of hydrogen by titanium dramatically increases once the protective oxide film normally present on the metal is damaged through either mechanical abrasion or chemical reduction. Hydrogen intake is accelerated by the presence of surface contaminants, including iron smears, and occurs predominantly as temperatures exceed 70 °C (160 °F).

Hydrating can be minimized by anodizing or thermal oxidizing treatments to increase the thickness of the protective oxide film. If it is impractical to apply these treatments, acid pickling of titanium components – with 10 to 30 vol.% nitric acid containing 1 to 3 vol.% hydrofluoric acid at 49 to 52 °C (120 to 125 °F) for 1 to 5 min – can be performed to remove iron smears. Acid pickling is also recommended for cleaning titanium components after inspection and repairs during shut-downs, especially components exposed to concentrated acetic acid in certain petrochemical operations.

To minimize hydrogen pickup during pickling, the volume ratio of nitric acid to hydrofluoric acid should be near 10. In some highly aggressive process environments, titanium components may have to be electrically insulated from more anodic components, such as aluminum, to prevent hydride formation as a result of hydrogen evolution on titanium surfaces. When process streams contain a significant volume of hydrogen (for example, reactor effluent from hydrotreatment units), titanium should be used only at temperatures below 175 °C (350 °F). Figure 2.8 shows crack extension versus time for hydrogen–oxygen mixtures.

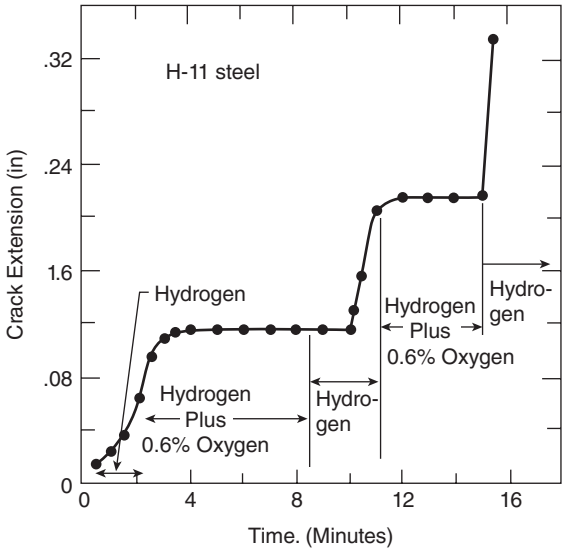


Figure 2.8 *Crack extension vs. time for hydrogen–oxygen mixtures. (Reproduced from H Barthelemy, 2011, with permission from the International Journal of Hydrogen Energy.)*

2.1.6.2 Hydrogen Blistering

Hydrogen blistering has been a problem primarily in the vapor recovery (light ends) section of catalytic cracking units and, to a lesser degree, in the low-temperature areas of the reactor effluent section of hydrotreating and hydrocracking units. Hydrogen blistering has also been seen in the overhead systems for sour water stripper towers and amine regenerator (stripper) towers, as well as in the bottom of amine contactor (absorber) towers.

Hydrogen blistering often accompanies hydrogen embrittlement as a result of aqueous sulfide corrosion. As a rule, the severity of hydrogen blistering depends on the severity of corrosion, but even low corrosion rates can produce enough hydrogen to cause extensive damage. In some cases hydrogen blistering is limited to dirty steel with highly oriented slag inclusions or laminations. Vapor/liquid interface areas in equipment often show most of the damage.

The basic approach toward reducing corrosion and hydrogen blistering in the various vapor-compression stages of catalytic cracking units should be aimed at decreasing the concentration of cyanide and disulfide ions in water condensate. Several methods for accomplishing this have been tried over the years.

Conversion of cyanide to harmless thiocyanate (SCN^-) by injection of air or polysulfide solutions at various locations has often produced undesirable side effects, such as accelerated corrosion and fouling at stagnant-flow areas. In contrast, water washing of the compressed wet-gas streams, in conjunction with corrosion inhibitor injection, has been found to be very effective when applied correctly and consistently.

Water washing reduces the concentration of cyanides by improved contacting of vapors and dilution of water condensate. To prevent dissolved and suspended solids from fouling the compressor aftercooler, only water of fairly good quality, such as boiler feed water or steam condensate, should be injected. To reduce the amount of freshwater used, stripping-stream condensate from the reflux drum can be used. As a rule, there is sufficient stripping-stream condensate to meet the wash-water requirements.

It is important that the waste sour water from the interstage and high-pressure separator drums be sent directly to waste disposal rather than first being recycled to the reflux drum. Waste water is often recycled for convenience so that its pressure can be reduced in the reflux drum prior to disposal. This alleviates the need for an external depressurizing drum, but will build up the concentration of ammonia, hydrogen sulfide, and, especially, hydrogen cyanide in the wet gas leaving the reflux drum. Consequently, excessive concentrations of cyanides will be found in water condensing in the high-pressure stage.

Water washing of the overhead systems of debutanizers and depropanizers is indicated only if serious fouling problems occur. Normally, these streams are quite dry and should be kept that way to minimize corrosion and hydrogen blistering problems. With proper water washing of the compressed wet-gas stream, water washing of the overhead vapor streams of the debutanizer and depropanizer towers becomes unnecessary.

Corrosion inhibitors help control aqueous sulfide corrosion and hydrogen blistering even though cyanides may still be present. Hydrogen activity probes and chemical testing of water condensate are used to monitor the effectiveness of water washing and inhibitor injection. Where limited hydrogen blistering occurs in certain components of hydrotreating and hydrocracking units, it is usually sufficient to line affected areas with stainless steel or alloy 400 (N04400). This also applies to components of overhead systems for sour water stripper towers and amine regenerator (stripper) towers, or to the bottoms of amine contactor (absorber) towers.

2.1.6.3 Hydrogen Stress Cracking

Sour water containing hydrogen sulfide can cause spontaneous cracking of highly stressed high-strength steel components, such as bolting and compressor rotors. Cracking has also occurred in carbon steel components containing hard welds. Hydrogen stress cracking was first identified in the production of sour crude oils when high-strength steels used for wellhead and down-hole equipment cracked readily after contacting produced water that contained hydrogen sulfide.

Hydrogen stress cracking (Figure 2.9) was not experienced by refineries in the gas industry and in petrochemical plants until the introduction of high-pressure processes that required high-strength bolting and other components in gas compressors. With the increased use of submerged arc welding for pressure vessel construction it was found that weld deposits significantly harder and stronger than the base metal could be produced. This led to transverse cracking in the weld deposit.



Figure 2.9 *Typical hydrogen stress corrosion cracking. (Reproduced with permission from Analog © Luis Orozco.)*

In general terms, hydrogen stress cracking occurs in the same corrosive environments that lead to hydrogen embrittlement. Hydrogen sulfide affects the corrosion rate and the relative amount of hydrogen absorption, but otherwise does not appear to be directly involved in the cracking mechanism. As a general rule of thumb, hydrogen stress cracking can be expected to occur in process streams containing in excess of 50 ppm hydrogen sulfide (although cracking has been found to occur at lower concentrations).

There is a direct relationship between hydrogen sulfide concentration and the allowable maximum hardness value of the heat-affected zone (HAZ) on one hand and cracking threshold stress on the other. Typically, the allowable maximum hardness value decreases 30 HB, and the allowable threshold stress decreases by 50% for a tenfold increase in hydrogen sulfide concentration.

An addition, hydrogen stress cracking occurs primarily at ambient temperatures. As in the case of hydrogen embrittlement and hydrogen blistering, hydrogen stress cracking of steel in refineries and petrochemical plants often requires the presence of cyanides.

The most effective way of preventing hydrogen stress cracking is to ensure that the steel is in the proper metallurgical condition. This means that weld hardness is limited to 200 HB. Because hard zones can also form in the HAZs of welds and shell plates from hot forming, the same hardness limitation should be applied in these areas. Guidelines for dealing with the hydrogen stress cracking that occurs in refineries and petrochemical plants are given in NACE RP 0472-2000.

Post-weld heat treatment of fabricated equipment will greatly reduce the occurrence of hydrogen stress cracking. The effect is twofold: First, there is the tempering effect of heating to 620 °C (115 °F) on any hard micro-structure, and second, the residual stresses from welding or forming are reduced. The residual stresses represent a much larger strain on the equipment than internal pressure stresses.

A large number of the ferrous alloys, including the stainless steels, as well as certain nonferrous alloys, are susceptible to hydrogen stress cracking. Cracking may be expected to occur with carbon and low-alloy steels when the tensile strength exceeds 620 MPa (90 ksi). Because there is a relationship between hardness and strength in steels, the above strength level approximates the 200 HB hardness limit. For other ferrous and non-ferrous alloys used primarily in oil field equipment, limits on hardness and/or heat treatment have been established in NACE MR 0175/ISO 15156-2003. Although oil field environments can be more severe than those encountered during refining, the recommendations can be used as a general guide for material selection

2.2 Hydrogen Attack

High-temperature hydrogen attack (HTHA) is a form of degradation caused by hydrogen reacting with carbon to form methane in a high-temperature environment.

$$C + 4H \rightarrow CH_4 \tag{2.4}$$

The methane forms and stays in grain boundaries and voids; however, it does not diffuse out of the metal. Once accumulated in the grains and voids, it expands and forms blisters, weakens the metal strength, and initiates cracks in the steel.

High-strength low-alloy steels are particularly susceptible to this mechanism, which leads to embrittlement of the bulk parent metal (typical C-0.5 Mo steels). The embrittlement in the material can result in a catastrophic brittle fracture of the asset.

Figure 2.10 is a picture of Blistering in metal due to HTHA.

The term hydrogen attack (or, more specifically, high-temperature hydrogen attack) refers to the deterioration of the mechanical properties of steels in the presence of hydrogen gas at elevated temperatures and pressures. Although not a corrosion phenomenon in the usual sense, hydrogen attack is potentially a very serious problem with regard to the design and operation of refinery equipment



Figure 2.10 *Blistering in metal due to high temperature hydrogen attack. (Reproduced with permission from Daubert Cromwell.)*

in hydrogen service. It is of particular concern in hydrotreating, reforming, and hydrocracking units at above about 260 °C (500 °F) and hydrogen partial pressures above 689 kPa (100 psia). Hydrogen attack takes the form of overall decarburization rather than blistering or cracking.

The overall effect of hydrogen attack is the partial depletion of carbon in pearlite (decarburization) and the formation of fissures in the metal. Hydrogen attack is accompanied by loss of tensile strength and ductility. Consequently, unexpected failure of equipment without prior warning signs is the primary cause for concern.

2.2.1 Forms of Hydrogen Attack

Hydrogen attack can take several forms within the metal structure, depending on the severity of the attack, stress, and the presence of inclusions in the steel. The following discussion will illustrate these. General surface attack occurs when equipment that is not under stress is exposed to hydrogen at elevated temperatures and pressures. As a rule, decarburization is not uniform across the surface or through the thickness; instead, it takes place at various locations within the structure.

Hydrogen attack often initiates at areas of high stress or stress concentration in the steel because atomic hydrogen preferentially diffuses to these areas. Isolated fingers of decarburized and fissured material are often found adjacent to weldments and are associated with the initial stages of hydrogen attack. It is also evident that the fissures tend to be parallel to the edge of the weld rather than the surface. This orientation of fissures is probably the result of residual stress next to the weldment. Fissures in this direction can form through-thickness cracks.

The necessary stress for inducing localized hydrogen attack is not limited to weldments. Hydrogen attack has been found to be concentrated at the tip of a fatigue crack that initiated at the toe of a fillet weld and propagated along the HAZ of the weld. In this case, the hydrogen-containing process stream evidently entered the fatigue crack and caused fissuring around the tip. Although no evidence of attack was found in adjacent portions of the piping system, the localized attack was the cause of a major failure.

Severe hydrogen attack can result in blisters and laminations. This is an advanced stage of hydrogen attack, and it is accompanied by complete decarburization throughout the cross section of the steel. The laminar nature of the fissures is typically obtained when no local stresses are present, but the physical appearance of this blistering is quite similar to hydrogen blistering (described earlier).

2.2.2 Prevention of Hydrogen Attack

The only practical way to prevent hydrogen attack is to use only steels that, based on plant experience, have been found to be resistant to this type of deterioration. The following general rules are applicable to hydrogen attack:

- Carbide-forming alloying elements, such as chromium and molybdenum, increase the resistance of steel to hydrogen attack.
- Increased carbon content decreases the resistance of steel to hydrogen attack.
- Heat-affected zones are more susceptible to hydrogen attack than the base or weld metal.

For most refinery and petrochemical plant applications, low-alloy chromium- and molybdenum-containing steels are used to prevent hydrogen attack. However, questions have recently been raised regarding the effect of long-term hydrogen exposure on C-0.5 Mo steel. As a result, low-alloy steels are preferred over C-0.5 Mo steel for new construction.

The conditions under which different steels can be used in high-temperature hydrogen service are listed in API 941. The principal data are presented in the form of Nelson curves, as shown in Figure 2.11. The curves are based on long-term refinery experience, rather than on laboratory studies and are periodically revised by the API Subcommittee on Materials Engineering and Inspection. The latest edition of API 941 should be consulted to ensure that the proper steel is selected for the operating conditions encountered.

In addition to hydrogen attack, hydrogen stress cracking can occur at carbon and low-alloy steel welds that have been in hydrogen service above approximately 260 °C (500 °F). Cracking is intergranular and typically follows lines of high, localized stress and/or hardness. Cracking is caused by dissolved hydrogen and is prevented by post-weld heat treatment. Proper hydrogen outgassing procedures should be followed when equipment is depressurized and cooled prior to shut-down.

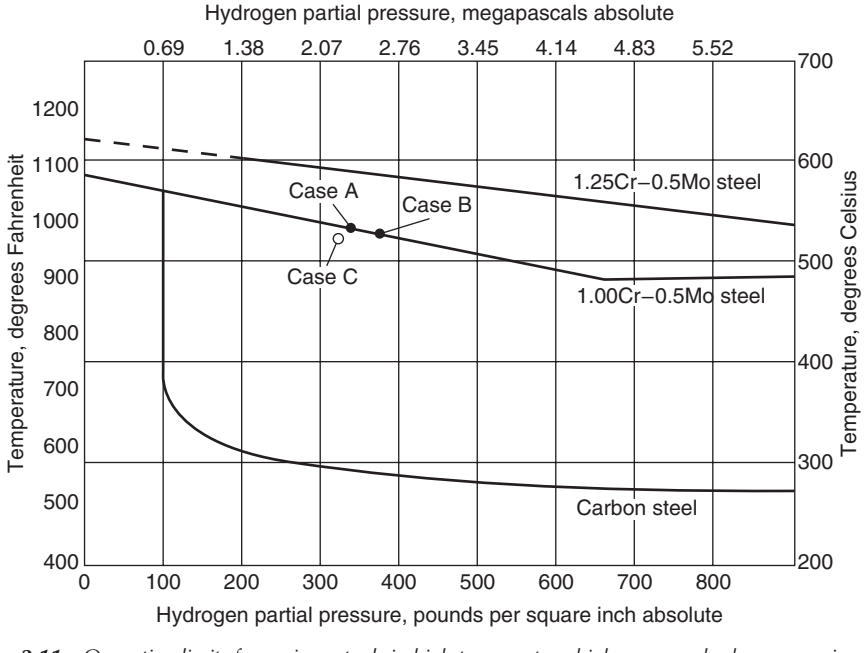


Figure 2.11 *Operating limits for various steels in high-temperature high-pressure hydrogen service (Nelson curves) to avoid decarburization and fissuring. (Reproduced with permission from Daubert Cromwell.)*

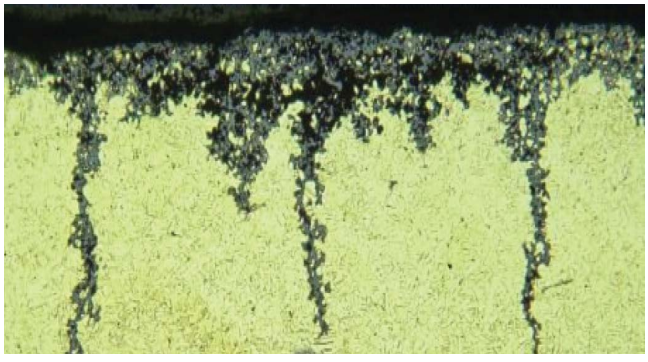


Figure 2.12 *Corrosion fatigue cracks on the inside diameter of a Admiralty brass exchanger tube. (Reproduced with permission from Daubert Cromwell.)*

Stainless steels with chromium contents above 12% and, in particular, the austenitic stainless steels are immune to hydrogen attack. It should be noted, however, that atomic hydrogen will diffuse through these steels; as a result, they will not provide protection against hydrogen attack if applied as a loose lining or an integral cladding over a non-resistant base steel.

2.3 Corrosion Fatigue

Corrosion, in conjunction with cyclic stressing, can bring about a significant reduction in the fatigue life of a metal. Failure under these circumstances is described as corrosion fatigue. Rotating equipment, valves, and some piping runs in refineries and petrochemical plants may be subject to corrosion fatigue. In particular, pump shafts and various springs are the two most likely candidates for corrosion fatigue. The types of springs involved include those of scraper blade devices in a wax production unit, internal springs in relief valves, and compressor valve springs.

Figure 2.12 shows corrosion fatigue cracks on the inside diameter of a Admiralty brass exchanger tube.

2.3.1 Prevention of Corrosion Fatigue

A number of corrective procedures are available for preventing corrosion fatigue. These include increasing the fatigue resistance and corrosion resistance of the metal involved, reducing the number of stress cycles or the stress per cycle, and removing or inhibiting the corrosive agent in the environment. Fatigue life can often be increased through heat treatments or alloy changes, which make the metal stronger and tougher.

Corrosion resistance can be improved by applying protective coatings or by a material change. A design change can eliminate vibration or (in a spring) reduce the stress per cycle. Finally, adding a corrosion inhibitor or removing a source of pitting, such as chlorides, can often increase the corrosion fatigue life of the failing part.

2.4 Liquid-Metal Embrittlement

Although liquid-metal embrittlement has been recognized for at least 50 years, it has received far less attention than the more commonly encountered hydrogen embrittlement or stress-corrosion cracking.

This is due in part to the fact that the probability of liquid-metal contact occurring in refineries and petrochemical plants is normally rather small.

In situations in which liquid-metal embrittlement has occurred, it has been mainly due to the zinc embrittlement of austenitic stainless steels. Isolated failures have been attributed to welding in the presence of residues of zinc-rich paint or to the heat treating of welded pipe components that carried splatters of zinc-rich paint. However, most of the reported failures due to zinc embrittlement have involved welding or fire exposure of austenitic stainless steel in contact with galvanized steel components.

For example, in one case, severe and extensive cracking in the weld HAZ of process piping made from austenitic stainless steel occurred in a petrochemical plant during the final stages of construction. Much of the piping had become splattered with zinc-rich paint. Although the welders had been instructed to clean affected piping prior to welding, no cleaning and only limited grinding was performed. After welding, dye penetrant inspection revealed many thin, branched cracks in the HAZ of welds.

In many cases, through-wall cracks cause leaks during hydrotesting. Typically, zinc embrittlement cracks contain zinc-rich precipitates on fracture surfaces and at the very end of the crack tip. Cracking is invariably intergranular in nature.

Zinc embrittlement is a relatively slow process that is controlled by the rate of zinc diffusion along austenitic grain boundaries. Zinc combines with nickel, and this results in nickel-depleted zones adjacent to the grain boundaries. The resulting transformation of face-centered cubic austenite to body-centered cubic ferrite in this region is thought to produce not only a suitable diffusion path for zinc, but also the necessary stresses for initiating intergranular cracking. Externally applied stresses accelerate cracking by opening prior cracks to liquid metal.

Although the melting point of zinc is 420 °C (788 °F), no zinc embrittlement has been observed at temperatures below 570 °C (1380 °F), probably because of phase transformation and diffusion limitations. There is no evidence that an upper temperature limit exists. In the case of zinc-rich paints, only those having metallic zinc powder as a principal component can cause zinc embrittlement of austenitic stainless steels. Paints containing zinc oxide or zinc chromates are known not to cause embrittlement.

2.4.1 Prevention of Zinc Embrittlement

Obviously, the best approach to the prevention of zinc embrittlement is to avoid or minimize zinc contamination of austenitic stainless steel components in the first place. In practice, this means using no galvanized structural steel, such as railings, ladders, walkways, or corrugated sheet metal, at locations where molten zinc is likely to drop on stainless steel components if a fire occurs.

If zinc-rich paints will be used on structural steel components, shop priming is preferred. Field application of zinc-rich paints should be done after all welding of stainless steel components has been completed and after insulation has been applied. Otherwise, stainless steel components should be temporarily covered with plastic sheathing to prevent deposition of overspray and splatter.

If stainless steel components have become contaminated despite these precautionary measures, proper cleaning procedures must be implemented. Visible paint overspray should be removed by sandblasting, wire brushing, or grinding. The operations should be followed by acid pickling and water rinsing. Acid pickling will remove any traces of zinc that may have been smeared into the stainless steel surface by mechanical cleaning operations. Suitable acid pickling solutions include 5 to 10% nitric acid, phosphoric acid, or sulfuric acid. Hydrochloric acid should not be used in order to avoid potential pitting or SCC problems. After removal of all traces of acid by water rinsing, final cleaning with naphtha solvent should be performed immediately before welding.

2.5 Basic Definition of Erosion-Corrosion

Various materials of construction for refinery and petrochemical plant service may exhibit accelerated metal loss under unusual fluid-flow conditions. Attack is caused by a combination of flow velocity (mechanical factors) and corrosion (electrochemical factors) known as erosion-corrosion.

Affected metal surfaces will often contain grooves or wave-like marks that indicate a pattern of directional attack. Soft metals, such as copper and aluminum alloys, are often especially prone to erosion-corrosion, as are metals such as stainless steels, which depend on thin oxide films for corrosion protection.

Most cases of erosion-corrosion can be mitigated by proper design and/or material changes. For example, by eliminating sharp bends, erosion-corrosion problems can be significantly reduced in process piping. Increasing the pipe diameter of vapor lines will reduce flow velocities and therefore erosion-corrosion by impinging droplets of liquid. Piping immediately downstream of pressure letdown valves often must be upgraded to prevent accelerated attack due to high flow turbulence.

2.5.1 Cavitation

Cavitation damage is a fairly common form of erosion-corrosion of pumps, impellers or hydraulic turbine internals. Cavitation is caused by collapsing gas bubbles at high-pressure locations; adjacent metal surfaces are damaged by the resultant hydraulic shock waves. Cavitation damage is usually in the form of loosely spaced pits that produce a roughened surface area.

Subsurface metal shows evidence of mechanical deformation. As a general rule, cast alloys are likely to suffer more damage than wrought versions of the same alloy. Ductile materials, such as wrought austenitic stainless steels, have the best resistance to cavitation.

Damage can be reduced by design changes, material changes, and the use of corrosion inhibitors. Smooth finishes on pump impellers will reduce damage. Some coatings can be beneficial. Design changes with the objective of reducing pressure gradients in the flowing liquid are most effective.

2.6 Mixed-Phase Flow

Accelerated corrosion due to mixed vapor/liquid streams is found primarily in crude and vacuum furnace headers and in transfer lines of crude distillation units, in overhead vapor lines and condenser inlets on various fractionation towers, and in reactor effluent coolers of hydrocracking and hydrotreating units.

In general, increases in vapor load and mass velocity increase the severity of high-temperature sulfidic corrosion by crude oils and atmospheric residuum (reduced crude). Corrosion is least severe with flow regimes in which the metal surface is completely wetted with a substantial liquid hydrocarbon layer. Corrosion is most severe with the spray flow that results from vapor velocities above 60 m/s (200 ft/s) and vapor loads above 60%.

Under these conditions, corrosion rates of certain components, such as furnace headers, furnace-tube return bends, and piping elbows, could increase by as much as two orders of magnitude. This phenomenon is caused by droplet impingement, which destroys the protective sulfide scale normally found on steel components. Such impingement damage is usually not seen in straight piping, except immediately downstream of circumferential welds. Damage is usually in the form of sharp-edged lake-type corrosion that, because of its appearance, is often confused with naphthenic acid corrosion.

As a rule, 5 Cr-0.5 Mo steel components have sufficient resistance to all but severe cases of droplet impingement in transfer lines. Higher alloys should be used for furnace tubes and associated components, such as headers and return bends.

Corrosion damage at elbows of overhead vapor lines is often caused by droplet impingement as a result of excessively high vapor velocities. Typical impingement-type corrosion of tubes and baffles occurs just below the vapor inlet of overhead condensers. As a general rule, overhead vapor velocities should be kept below 7.5 m/s (25 ft/s) to minimize impingement-type corrosion. In addition, horizontal impingement baffles can be mounted just above the top tube row of overhead condensers.

Air-cooled reactor effluent coolers of hydrocracking and hydrotreating units are also prone to impingement-type corrosion. Poor flow distribution through large banks of parallel air coolers can result in excessive flow velocities in some coolers, usually those in the center. The resulting low flow velocities in the outer coolers can cause deposition of ammonium sulfide and/or chloride in these coolers; this blocks the tubes and further increases velocities in the remaining air coolers.

This problem is aggravated by low, night-time air temperatures, which increase deposition problems. Installation of protective sleeves (ferrules) at the inlet tube end has helped to reduce attack in some cases; in others, it has only moved the area of attack to an area immediately downstream of the sleeves. Careful attention to proper flow distribution through redesign of the inlet headers is often the only way of controlling air cooler corrosion.

2.7 Entrained Catalyst Particles

Accelerated corrosion due to entrained catalyst particles can occur in the reaction and catalyst regeneration sections of catalytic cracking units. Refractory linings are required to provide protection against oxidation and high-temperature sulfidic corrosion, as well as erosion by catalyst particles, particularly in cyclones, risers, standpipes, and slide valves.

Stellite hard facing is used on some components to protect against erosion. When there are no erosion problems and when protective linings are impractical, austenitic stainless steels such as Type 304 (S30400) can be used. Cyclone dip legs, air rings, and other internals in the catalyst regenerator are usually made of Type 304 (S30400) stainless steel, as is piping for regenerator flue gas.

The main fractionation tower is usually made of carbon steel, with the lower part lined with a ferritic or martensitic stainless steel containing 12% Cr such as Type 405 (S40500) or 410 (S41000). Slurry piping between the bottom of the main fractionation tower and the reactor may receive an additional corrosion allowance as protection against excessive erosion.

2.8 Systematic Analysis of Project

Where corrosion can interfere, the true functional purpose will not be achieved. Thus concerned designers should not concentrate purely on the functional aspects of design, to the total exclusion of other considerations, but must be aware that there are many ways in which corrosion can ruin even the best creation.

Designers should acquaint themselves with the basics of corrosion and should be fully aware of their own power and opportunity to ease, retard, or stop corrosion in a reasonable and economic way, by selective employment of qualified precautions or by optimal adjustment of the functional design. The corrosion-control measures they take in their designs need tactical, logistic, and mainly logical support embodied in the design itself. Designers should appreciate both the technical formulae and the corrosion that destroys the function of the product. All this knowledge should be combined in a unified and orderly form of creation. Basically, the main effort in corrosion control is given to:

- curative control – to repair corrosion after it has occurred,
- preventive control – to avoid or delay corrosion and reduce its harmful effects by taking precautions in advance.

Preventive control deals with the following:

- Pre-production planning
- Specification of corrosion-control measures and selection of optimal materials
- Design forms
- Fabrication and treatment methods to suit the finite environment
- Conditions of employment.

Further, preventive control is concerned with putting these selected measures into effect prior to deployment of the designed structure or equipment, and ultimately with the means of securing the appropriate quality for the economically extended functionalism of the product.

The cost and degree of efficiency of the embodied corrosion-control measures can be predetermined and their system varied to suit. The unexpected is more expensive than the planned and predicted. For this reason preventive control should be the prime consideration of every designer. On the other hand, curative control of the designed utility must not be altogether forgotten and all newly designed products must be made ready for its probable deployment at any appropriate time.

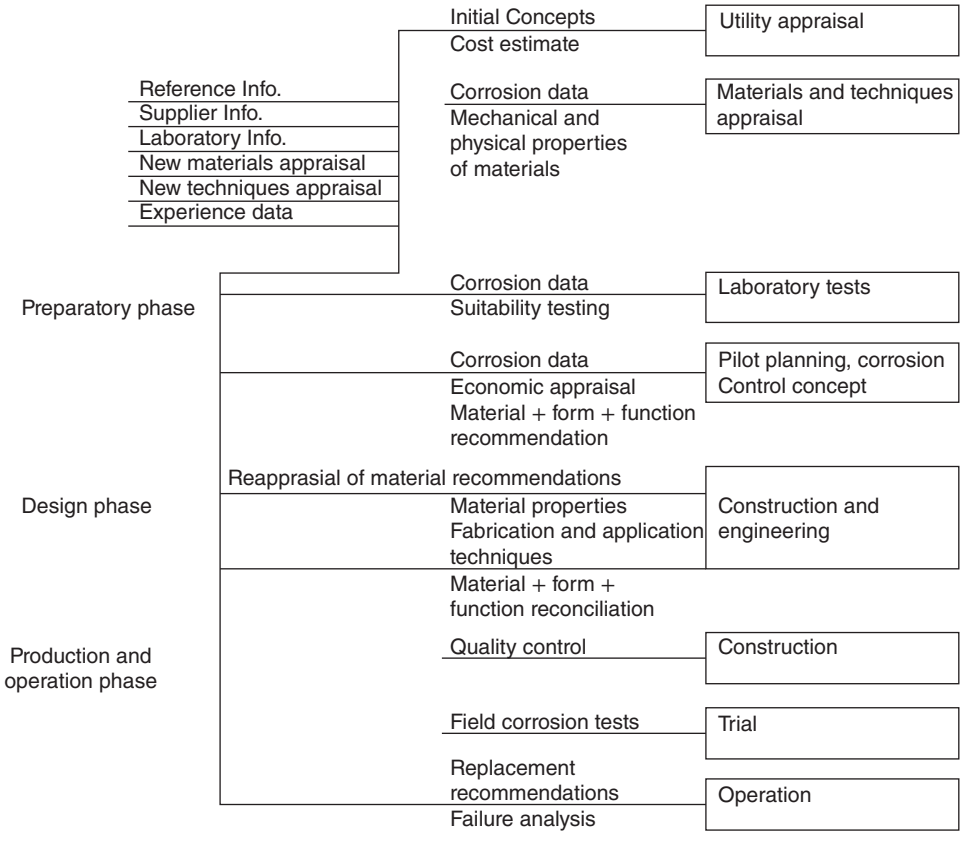


Figure 2.13 *Schematic diagram of corrosion control in design.*

2.8.1 Organization of Work

A thorough planning of working sequences and procedures is necessary to secure the requisite efficiency and smooth flow of applying corrosion control in design. Possible extent, sequencing, and flow are indicated in a schematic diagram of corrosion control (Figure 2.13).

2.8.2 Teamwork

Close cooperation between the executive management, designers, and corrosion experts is a necessity. In a responsible engineering practice, corrosion control can no longer be fully subordinate to the others – it must be an equal member of the team.

The team consists of:

- Development engineer
- Economist
- Estimators and costing personnel
- Designers
- Draughtsman
- Production control
- Corrosion engineer
- Laboratories and testing establishments
- Industry related to corrosion data
- Quality control organization.

The following show what kind of cooperation these specialists can expect from any other member of his corrosion control team:

- Development engineer
  - Informs on overall corrosion involvement within the project utility.
  - Informs on probable or possible environmental conditions, and corrosion and ecological problems created by the product.
- Economist
  - Informs on broad spectrum evaluation of economic feasibility of the product, including its corrosion control.
  - Instructs on cost limits for implementation of corrosion-control measures. In the latter stages provides budgetary control to prevent corrosion control from running wild and to prevent unnecessary and excessive precautions.
- Estimators and costing personnel
  - Compute, financially evaluate, record, and report continuously on the cost of anti-corrosion measures at all stages of the design work, to prevent waste.
- Designers
  - Study, consider, reconcile, and embody into the design such corrosion-control precautions that materially do not interfere with the engineering function of the utility and serve the purpose of optimal upkeep of its economic function.
  - Seek relevant information from corrosion specialists, and other involved personnel and sources on matters of corrosion-control policy and details.

- Supply corrosion specialists with the necessary data and allow access to their work for the purpose of study and constructive criticism.
- Amend, revise or modify their design to a reasonable degree to suit the demands of corrosion control (changes to be documented).
- Implement the design instructions with well-founded quality control rules on matters of corrosion prevention.
- Supply required data to budgetary control for costing and evaluation of corrosion prevention.
- Initiate procurement or contract documents assisting in optimal corrosion control.
- Secure compatibility and prevent corrosive interference within their design between items supplied from various sources.

- Draughtsman
  - Study and correctly interpret corrosion-control instructions and involvement of guidance drawings, specifications, and design and quality control instructions.
  - Consult with corrosion specialists on inclusion of relative aspects of corrosion control in the working drawings, bills of materials, and schedules in the best interest of preventing infusion of corrosion into the product to be fabricated.
  - Co-operate with production control on adjustment of corrosion-prevention measures to suit both parties and amend working drawings and schedules accordingly.
  - Supply necessary data to costing personnel.
  - Assist corrosion specialist in evaluation of drafting work.
  - Production control
  - Secure practical planning of corrosion-control measures to suit the design and the particular production methods and techniques, as well as the application facilities and procedures.
  - Reconcile the design with production.

- Corrosion engineer
  - Supplies up-to-date information and practical expert advice (discussions, evaluations, advisory worksheets, design instructions, proposals, and specifications) on the principles and good practice of corrosion control; on the nature and effect of corrosive environments; on structural, metallurgical, physical, and mechanical properties of various materials relative to their rate of corrosion, on their availability, fabrication, welding, treatment, their optimum design form, method of applicationand effective saving in weight.
  - Advises on substitutions, clad metals, weld overlays, metallizing, preservation systems, anodic and cathodic protection, environmental adjustment, etc.
  - Acts as a clearing house for corrosion information to feed it selectively to the design personnel and to foster their awareness and involvement in corrosion control. Participates in writing specifications, standards, and recommended practice instructions on matters of corrosion-control affinity.
  - In collaboration with laboratories, testing establishments, and project officers investigates new corrosion-control materials, processes, equipment, and methods consistent with good practice; generates new ideas and investigates changes in design, specifications and standards.
  - Evaluates economy of individual precautions on demand.
  - Correlates technical work of design and drawing offices with original corrosion-control specifications, design instructions, manuals, standards, and rules of good husbandry in corrosion control; instructs and examines for correct incorporation of corrosion control in all design activities, including guidance and working drawings, either in pictorial form or in notes, schedules and bills of materials.

- Assists in translation of corrosion aspects of drawings and specifications into practical working instructions for project and production engineers and represents corrosion-control interests in negotiations between the design office and production organization for sound inclusion of corrosion-control rules, specifications, instructions, and quality control stipulations into production planning.
- Collaborates with the quality control organization on setting up of appropriate quality control procedures and on maintenance of quality assurance of corrosion-control precautions during design, drafting, production, and trial activities.
- Represents management and design office on corrosion and failure committees for interpretation of applied corrosion-control measures and proposes revisions.
- Co-operates with ordering channels on corrosion-control suitability of bought-in items and appropriate instructions contained in contracting documents.
- Laboratories and testing establishments
- Report on pure research of corrosion phenomena and applied research of corrosion-control materials and methods.
- Test at various stages of the design program, or on request, the performance and suitability of materials and methods to assure optimum use, application, and design form in the given conditions.
- Participate in pilot and trial runs for evaluation of efficiency or merit of tested corrosion-control precautions.
- Install and operate scientific testing and recording apparatus for evaluation of failures and nondestructive testing.
- Participate in quality assurance.
- Assist the design organization in avoidance of guesswork in preparation of design and in establishing a more stable scientific basis for engineering decisions.

- Industry, related to corrosion data

  - Supplies accurate and complete corrosion data on their own products, methods, techniques, and facilities. Collaborates on applied corrosion research and testing relevant to their products.
  - Supplies correct materials and services in accordance with specifications, design, schedules, and working drawings, and maintains their uniform quality.
  - Trains and supplies efficient advisory staff, approved contractors, and site inspectors to secure effective corrosion-control measures (materials and work) when arranged.

- Quality control organization

  - Assures that quality control measures are maintained at all levels of planning, design, drawing, and fabrication.
  - Plans and organizes quality control for individual corrosion-control systems and procedures.
  - Composes written or drawn instructions and quality assurance specifications overall or in detail for individual tasks.
  - Performs practical inspections in cooperation with laboratories and corrosion specialists.
  - Indicates modes of enforcement of quality assurance.

2.8.3 Sources of Information

Before project analysis can commence, the basic common concepts of the project utility should be known to all personnel engaged both in functional design and corrosion-control work, as well as the basic philosophy of the utility complex, and the principles of working and flow sequences of all mechanical, chemical, and electronic components that constitute the utility.

Further, the design personnel should endeavor to collect from all available sources accurate data and information relating to corrosion-control requirements of the project, in their most comprehensive form, to allow the designers to analyze and select proper measures and appreciate accurately their probabilities.

2.8.4 Environmental Conditions

The environmental conditions include a thorough review of corrosive environments existing in the oil, gas, and petrochemical industries, and can be classified as follows:

- *Atmospheric environment*. The atmospheric environment is defined under categories of dry, damp, humid, rural, industrial, coastal, municipal, etc. Generally an increase in humidity, temperature, and the percentage of acid gases such as $CO_2, H_2S, SO_2, CO, Cl_2$ will increase the corrosivity (for more information see API Standard 571 7 580).
- *Natural waters*. The corrosivity of natural waters depends on their constituents, such as dissolved solids, gases, and sometimes colloidal or suspended matter. The effects may either stimulate or suppress the corrosion reaction. Constituents or impurities in water include dissolved gases such as oxygen, CO_2, SO_2, NH_3, H_2S, some of which are the result of bacterial activity. Dissolved mineral salts are mostly calcium, magnesium sodium, bicarbonate, sulfate, chloride, and nitrate. The effect of each of these ions on corrosion rate is different, but the chlorides have received the most study in this regard. Organic contaminants of water can directly affect the corrosion rate of metals and alloys. Bacteria, under optimum conditions can double their number in 10–60 minutes. This characteristic is typical of the widespread biodeterioration caused by microbes in all industries, of which corrosion is a special case. With a few exceptions such as synthetic polymers, all materials can be attacked by bacteria.
- *Seawater*. The greatest attack on offshore structures occurs in the splash zone due to alternate wetting and drying, and also aeration. In quite stagnant conditions the effect of bacteria and the pitting type of corrosion are predominant. The rapid growth of marine fouling in the tropics may provide a protective shield that counteracts the effect of the greater activity of the warmer water.
- *Soils*. Most of the industrial equipment in contact with soil or embedded underground will suffer corrosion. Increase in water content and decrease in pH and resistivity enhances the corrosivity of soil.
- *Chemicals*. Chemical environments are found mostly in petrochemical industries, but also in refineries and can be categorized as follows:
  - Type and composition of the chemical; physical state (solid, liquid, gaseous); toxicity; purity; concentration; pH value; continuity and type of exposure (cycling, immersion, spillage, fumes); maximum and minimum temperatures; fluid velocity; aeration and oxygen content; effect of corrosion products on the chemical; catalytic effect; probability of osmosis; etc.
  - To detail all the chemical environments and suitable materials is impossible because of the large amount of data. For example if some 400 systems are identified as being handled and processed on a large scale and there are 10 suitable materials, then 4000 systems would have to be considered. Since temperature concentration and solution velocity are important in determining corrosion rate, and if only five levels of each of the three variables are considered, then the number of environments to be considered would be $4000 \times 53 = 600\,000$. Therefore only those chemical environments that are corrosive and have a detrimental effect on material selection in the oil, gas, and petrochemical industries are briefly discussed.
- *Dry heat or cold exposure*. Maximum and minimum temperature; temperature gradient; temperature spread; frequency of variations; hot spots; etc.
- *Abrasion exposure*. Degree; duration; concentration; etc.

- *Microbiological influence*. Type of microbial life; direct or indirect effect; medium; temperature; periodicity of exposure; etc.
- *Shock and vibration*. Source; strength; frequency; concentration; transfer path; etc.
- *Atomic radiation*. Type; exposure; continuity; temperature; etc.
- *Absorbent materials*. Type (mortar, concrete, brick, floor compositions, wood, plastics, insulating and gasket materials, etc.); thickness; pH value; consistency; porosity; evaporation rate; absorbence rate; conductivity and resistivity; etc.

2.8.5 Case Histories and Technical Data Records

Historically documented cases of the corrosion behavior of the same or a similar product and of the effectiveness of corrosion-control methods applied in similar environmental and operational circumstances are very useful for comparative evaluation of corrosion control in design. Such information, however, should be studied and considered with caution, taking into account the possibility of many variations and combinations of conditions, from which errors and misconceptions could arise. Ultimately, each design case should be considered unique and no individual case history accepted as an unquestionable dictate.

2.8.5.1 Failure Reports

The negative information contained in these documents should be recorded in a comprehensive form (object, materials, fabrication, treatment, operational data, locality, description and cause of failure), evaluated either by corrosion experts or by a failure board, and filed for easy reference by all design personnel. The reports can either be filed individually or together. Where a number of failure reports on a related subject accumulate, a corrosion failure index dealing with various sections of the problem or various parts of the utility is preferred. Where there is a considerable number of failures of a comparatively restricted and repetitive nature, it is desirable to record such information by electronic data processing. It is important that such information, in accurate form and preferably converted into a useful summary, be distributed as soon as possible to all interested personnel to be used either for design revision or maintenance programming.

2.8.5.2 Materials and Treatment Records

Positive information recorded in an index form, and accurately updated, can illustrate the whole development and progress of corrosion-control application in the design of a particular project or part and may become a source of valuable information for corrosion-control design analysis, specifications, working drawings, schedules, standards and procedures.

2.8.5.3 Reference File

No person engaged in corrosion control should be without access to a filing system that covers accurately all relevant information on a particular enterprise; the volume of data required is too extensive to memorize. This can be achieved either by a well-organized personal file or through access to a large-scale or computerized filing system. The volume of such a file, in so far as it depends on the extent of activities, will not be static, but altogether dynamic; it will grow in size and utility with the demand and progress of corrosion science and art, and be immediately usable to cover the need of the moment and so allow an easy literature search.

2.8.5.4 Comparative index

When the extent of the reference file becomes too unwieldy for a quick search, or where several materials of the same generic group are often evaluated for preferential use, a comparative index can prove of value.

2.8.6 Analysis

Once the preparatory stage of corrosion-control work in design (i.e. setting up a suitable organization and assembling ample information) is complete, the design team may commence with a step-by-step evaluation of corrosion-control data, requirements, rules, and other relevant information in a suitable and systematic manner. The results of this analysis will be used to reconcile the arising corrosion-prevention ideas with the designers' functional engineering appreciation, in accordance with their merits. Finally an overall decision will be made and a plan of action compatible with the planned function, the utility's economic life and the safety of the utility or its parts agreed.

One may, however, consider, after a detailed examination of the schematic design control analysis and the following individual sections, that by completely separating these two efforts some work will be duplicated and valuable time wasted. Thus it may be left to the discretion of individual organizations in general, or to requirements of individual projects in particular, whether by a judicious combination of items, at least in some of the opposing sections of analysis, a method of parallel thinking can be developed and unnecessary repetition avoided.

Each individual item in the two main parts of design analysis is important, in order to secure the intended results, and should not be forgotten or neglected. For this reason a combined analytical effort should be suited to the project and systematically followed without fail.

One can mention here that the corrosion-control analysis does not absolve the designer from implementing the basic engineering requirements of the utility itself, and a correct corrosion-control decision must not obstruct the product's engineering function. Both are, however, so closely knitted together that they should be considered of equal importance, albeit on a selective basis. It is not good policy to consider only one branch of design analysis and neglect the other.

2.9 Forms of Corrosion and Preventive Measures

This section is specific to corrosion engineers and is a guide for the designers of petroleum equipment, production units, pipelines, refineries, petrochemicals, and related structures.

The purpose of corrosion consideration in design is to avoid or minimize corrosion hazards technically and economically, and to try to ensure a longer life for the selected materials and constructed structures and equipment.

The designer, material engineer, and corrosion engineer must work closely together to ensure that premature failure will not occur because of design defects or improper material selection.

Basic forms of corrosion and their prevention methods are discussed below for consideration during the design stages and to help the parties involved to analyze the project with respect to corrosion.

Eight forms of corrosion have been classified, in general based on the appearance of the corroded materials. Each form can be identified by visual observation. The naked eye may be sufficient, but sometimes magnification is helpful. Careful inspection of the corroded test specimens helps to solve corrosion problems and examination *before* cleaning is particularly desirable.

These eight more-or-less interrelated forms of corrosion are as follows:

- Uniform or general corrosion
- Galvanic or two-metal corrosion
- Crevice corrosion
- Pitting
- Intergranular corrosion
- Selective leaching or parting
- Erosion-corrosion
- Stress corrosion.

2.9.1 Uniform or General Corrosion

Uniform corrosion is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the total area. General thinning takes place until failure. On the basis of tonnage wasted, this is the most important form of corrosion.

However, uniform corrosion is relatively easily measured and predicted, making disastrous failures relatively rare. In many cases, it is objectionable only from an appearance standpoint. As corrosion occurs uniformly over the entire surface of the metal component, it can be practically controlled by cathodic protection, use of coatings or paints, or simply by specifying a corrosion allowance. In other cases, uniform corrosion adds color and appeal to a surface. Two classic examples in this respect are the patina created by naturally tarnishing copper roofs and the rust hues produced on weathering steels.

The breakdown of protective coating systems on structures often leads to this form of corrosion. Dulling of a bright or polished surface, etching by acid cleaners, or oxidation (discoloration) of steel are examples of surface corrosion. Corrosion-resistant alloys and stainless steels can become tarnished or oxidized in corrosive environments. Surface corrosion can indicate a breakdown in the protective coating system, however, and should be examined closely for more advanced attack. If surface corrosion is permitted to continue, the surface may become rough and surface corrosion can lead to more serious types of corrosion.

While this is the most common form of corrosion, it is generally of little engineering significance, because structures will normally become unsightly and attract maintenance long before they become structurally affected. The facilities shown in figure 2.14 show how this corrosion can progress if control measures are not taken.

2.9.1.1 Prevention

Uniform attack can be prevented or reduced by using:

- proper materials, including coatings,
- inhibitors,
- cathodic protection.

These expedients can be used singly or in combination.



Figure 2.14 *An example of uniform corrosion. (Reproduced with permission from Daubert Cromwell.)*

Table 2.1 *Standard emf series of metals*

Metal/metal ion equilibrium (unit activity)	Electrode potential vs. normal hydrogen electrode at 25 °C (volts)
Noble or cathodic	
Au/Au^{+3}	+1.498
$Pt–Pt^{+2}$	+1.2
Pd/Pd^{+2}	+0.987
Ag/Ag^{+}	+0.799
Hg/Hg_2^{+2}	+0.788
Cu/Cu^{+2}	+0.337
H_2/H^{+}	0.0
Active or anodic	
Pb/Pb^{+2}	−0.126
Sn/Sn^{+2}	−0.136
Ni/Ni^{+2}	−0.250
Co/Co^{+2}	−0.277
Cd/Cd^{+2}	−0.403
Fe/Fe^{+2}	−0.440
Cr/Cr^{+3}	−0.744
Zn/Zn^{+2}	−0.763
Al/Al^{+3}	−1.662
Mg/Mg^{+2}	−2.363
Na/Na^{+}	−2.714
K/K^{+}	−2.925

2.9.2 Galvanic or Two-Metal Corrosion

A potential (emf) difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or electrically connected), this potential difference produces an electron flow between them. Corrosion of the less corrosion-resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less-resistant metal becomes anodic and the more-resistant metal cathodic. Usually the cathode or cathode metal corrodes very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic or two-metal corrosion.

For simplicity, all potentials are referenced against the hydrogen electrode (H_2/H^{+}), which is arbitrary defined as zero.

The potential between metals exposed to solutions containing approximately one atom gram weight of their respective ions (unit activity) are precisely measured at constant temperature. Table 2.1 presents the standard emf series of metals.

The natural differences in metal potentials produce galvanic differences, such as the galvanic series in sea water. If electrical contact is made between any two of these materials in the presence of an electrolyte, current must flow between them. The farther apart the metals are in the galvanic series, the greater the galvanic corrosion effect or rate will be. Metals or alloys at the upper end are noble while those at the lower end are active. The more active metal is the anode or the one that will corrode.

Control of galvanic corrosion is achieved by using metals closer to each other in the galvanic series or by electrically isolating metals from each other. Cathodic protection can also be used to control galvanic corrosion effects.

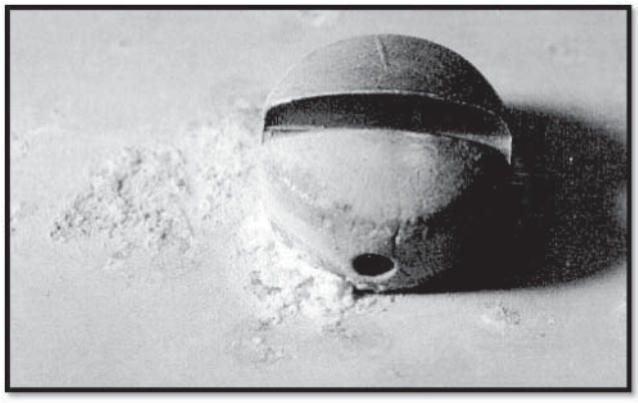


Figure 2.15 *An example of galvanic corrosion of aluminium. (Reproduced with permission from Daubert Cromwell.)*

Figure 2.15 shows the corrosion caused by a stainless steel screw causing galvanic corrosion of aluminium. The picture shows corrosion resulting from only six months exposure at the Atmospheric Test Site.

2.9.2.1 Prevention

For combating galvanic corrosion the following practices are useful:

- Select combinations of metals as close together as possible in the galvanic series.
- Avoid the unfavorable area effect of a small anode and large cathode. Small parts such as fasteners sometimes work well for holding less-resistant materials.
- Insulate dissimilar metals wherever practicable.
- Apply coating with caution.
- Add inhibitors, if possible, to decrease aggressiveness of the environment.
- Avoid threaded joints for materials far apart in the galvanic series.
- Design for the use of readily replaceable parts or make them thicker for longer life.
- Install a third metal that is anodic to both metals in the galvanic contact.

2.9.3 Crevice Corrosion

Intensive localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. The attack is associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads.

Figure 2.16 shows screws and fasteners that are common sources of crevice corrosion problems. The stainless steel screws shown corroded in the moist atmosphere of a pleasure boat hull.

2.9.3.1 Combating Crevice Corrosion

Methods and procedures for combating crevice corrosion are as follows:

- Use welded butt joints instead of riveted or bolted joints in new equipment.
- Close crevices in existing lap joints by continuous welding, caulking, or soldering.
- Design vessels for complete drainage; avoid sharp corners and stagnant areas.
- Inspect equipment and remove deposits frequently.

- Remove solids in suspension early in the process or plant flow sheet, if possible.
- Remove wet packing materials during long shut-downs.
- Provide uniform environments, if possible, as in the case of back-filling a pipeline trench.
- Use "solid" non-absorbent gaskets, such as teflon, whenever possible.
- Weld instead of rolling tubes, in tube sheets.

2.9.4 Pitting

Pitting is a form of extremely localized attack that results in holes or cavities in the metal with the surface diameter about the same as or less than the depth.

Pitting is one of the most destructive forms of corrosion; it causes equipment to fail because of perforation with only a small percentage weight loss from the entire structure. It may be considered as the intermediate stage between general overall corrosion and complete corrosion resistance. This is shown diagramatically in Figure 2.17.

Specimen A shows no attack whatsoever, specimen C has metal removed or dissolved uniformly over the entire exposed surface. Intense pitting occurred on specimen B at the points of breakthrough.

Oxidizing metal ions with chlorides are aggressive pitters. Cupric, ferric, and mercuric halides are extremely aggressive; even our most corrosion-resistant alloys can be pitted by $CuCl_2$ and $FeCl_3$.

Pitting corrosion can lead to unexpected catastrophic system failure. The split tubing in Figure 2.17 was caused by pitting corrosion of stainless steel.

2.9.4.1 Prevention

The methods suggested for combating crevice corrosion generally apply for pitting as well. Materials that show a tendency to pit during corrosion tests should not be used to build the plant under consideration. For example, the addition of 2% molybdenum to 18-8S (Type 304) to produce 18-8S Mo (Type 316) results a very large increase in resistance to pitting.

Various metals and alloys may be used as a qualitative guide to suitable materials, however tests should be conducted before a final selection is made. Adding inhibitors is sometimes helpful, but this may be a dangerous procedure unless attack is stopped completely. If it is not, the pitting may be increased.

Grain boundary effects are of little or no consequence in most applications or uses of metals. If a metal corrodes, uniform attack results since grain boundaries are usually only slightly more reactive



Figure 2.16 *Screws and fasteners that are common sources of crevice corrosion problems. (Reproduced with permission from Analog © Luis Orozco.)*

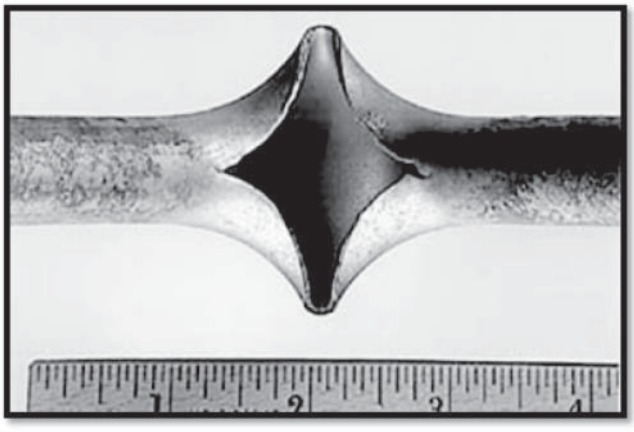


Figure 2.17 *Pitting corrosion of stainless steel. (Reproduced with permission from Analog © Luis Orozco.)*

than the matrix. However, under certain conditions, grain interfaces are very reactive and intergranular corrosion results.

Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is intergranular corrosion. The alloy disintegrates (grains fall out) and/or loses its strength. Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain boundary areas. A small amount of iron in aluminum, where the solubility of iron is low, has been shown to segregate into the grain boundaries and cause intergranular corrosion. It has been shown that based on surface tension considerations, the zinc content of a brass is higher at the grain boundaries. Depletion of chromium in the grain boundary regions results in intergranular corrosion of stainless steels.

2.9.4.2 Austenitic Stainless Steels

Numerous failures of 18-8 stainless steels (Type 304) have occurred because of intergranular corrosion. This happens in environments where the alloy is expected to exhibit excellent corrosion resistance. When these steels are heated in the temperature range 370–815 °C they become sensitized to intergranular corrosion. For example, with intentional sensitization by heating at 650 °C for 1 hour, the process of chromium depletion in the grain boundary can be shown. The chromium-depleted zone near the grain boundary is corroded because it does not contain sufficient corrosion resistance to resist attack, but chromium carbide ($Cr_{23}C_6$) is insoluble and precipitates. Therefore the steel is said to be sensitized to intergranular (intercrystalline) attack.

Note: The detrimental effect of carbon and nitrogen in ferrite can be overcome by changing the crystal structure to austenite, a face-centered cubic (fcc) crystal structure. This change is accomplished by adding austenite stabilizers, most commonly nickel, but also manganese and nitrogen. Austenite is characterized as non-magnetic.

2.9.4.3 Control for Austenitic Stainless Steels

Three methods are used to control or minimize intergranular corrosion of austenitic stainless steels:

- Employing high-temperature solution heat treatment, which is termed quench-annealing or solution quenching.
- Adding elements that are strong carbide formers (called stabilizers).
- Lowering the carbon content to below 0.03%.

2.9.4.4 Weld Decay

Many failures of 18-8 stainless steel occurred in the early history of this material until the mechanism of intergranular corrosion was understood. Failures still occur when this effect is not considered. These are associated with welded structures, and the material attacked intergranularly is called "weld decay."

2.9.4.5 Knifeline Attack

Knifeline attack (KLA) is similar to weld decay and they both result from intergranular corrosion and are associated with welding. The three major differences are:

- KLA occurs in a narrow band in the base metal immediately adjacent to the weld, whereas weld decay develops at an appreciable distance from the weld.
- KLA occurs in stabilized steels.
- The thermal history of the metal is different.

2.10 Selective Leaching or De-Alloying Corrosion

Selective leaching is the removal of one element from a solid alloy by corrosion processes. The most common example is the selective removal of zinc in brass alloys (dezincification). Similar processes occur in other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are removed.

Selective leaching is the general term that describes these processes, and its use precludes the creation of terms such as dealuminumification, decobaltification etc. "Parting" is a metallurgical term that is sometimes applied, but selective leaching is preferred.

2.10.1 Dezincification: Characteristics

Common yellow brass consists of approximately 30% zinc and 70% copper. Dezincification is readily observed with the naked eye because the alloy assumes a red or copper color that contrasts with the original yellow. There are two general types of dezincification and both are readily recognized. One is uniform or layer-type, and the other is localized or plug-type dezincification.

The process of extraction of a soluble component from an alloy with an insoluble component, by percolation of the alloy with a solvent – usually water.

2.10.1.1 Prevention

Dezincification can be minimized by reducing the aggressiveness of the environment (i.e. oxygen removal) or by cathodic protection, but in most cases these methods are not economical. Usually a less susceptible alloy is used. For example, red brass (15% Zn) is almost immune. Better brass is made by addition of 1% tin to a 70-30 brass (Admiralty metal). Further improvement is obtained by adding small amounts of arsenic, antimony or phosphorus as "inhibitors."

2.10.2 Graphitization

Gray cast iron shows the effect of selective leaching particularly in relatively mild environments. The cast iron appears to become "graphitized" in that the surface layer has the appearance of graphite and can be easily cut with a penknife. Based on this appearance, this phenomenon was christened

"graphitization." This is a misnomer because the graphite is present in the gray iron before corrosion occurs. It is also called "graphitic corrosion."

2.10.2.1 Prevention

It is recommended to use ductile (nodular) cast iron instead of gray cast iron (brittle). Ductile iron pipe with a cement mortar lining has given excellent performance.

2.11 Erosion-Corrosion

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities. This can be the result of fast fluid flow past a stationary object, as is the case with the oil-field check valve shown below, or it can result from the quick motion of an object in a stationary fluid, such as happens when a ship's propeller churns the ocean.

Erosion-corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface (see Figure 2.18). This movement is quite rapid, and mechanical wear effects or abrasion are involved. Metal is removed from the surface as dissolved ions, or it forms solid corrosion products that are mechanically swept from the metal surface. Sometimes movement of the environment decreases corrosion, particularly when localized attack occurs under stagnant conditions, but this is not erosion-corrosion because deterioration is not increased. Erosion-corrosion is characterized by grooves, gullies, waves, rounded holes, and valleys.

Most metals and alloys are susceptible to erosion-corrosion damage. Many depend upon the development of a surface film of some sort (passivity), for resistance to corrosion. Examples are aluminum, lead, and stainless steels. Erosion-corrosion results when these protective surfaces are damaged or



Figure 2.18 *An example of erosion-corrosion. (Reproduced with permission from Daubert Cromwell.)*

Table 2.2 *Corrosion of metals by seawater moving at different velocities*

Material	Typical corrosion rates (Mdd; weight loss in milligrams per square decimetre per day)		
	30.5 cm/s	122 cm/s	820 cm/s
Carbon steel	34	72	254
Cast iron	45	–	270
Silicon bronze	1	2	343
Admiralty brass	2	20	170
Hydraulic bronze	4	1	339
G bronze	7	2	280
Al bronze (10% Al)	5	–	236
Aluminum brass	2	–	105
90-10 Cu Ni (0.8% Fe)	5	–	99
70-30 Cu Ni (0.05% Fe)	2	–	199
70-30 Cu Ni (0.5% Fe)	< 1	< 1	39
Monel	< 1	< 1	4
Stainless steel Type 316	1	0	< 1
Hastelloy C	< 1	–	3
Titanium	0	–	0

worn and the metals or alloys are attacked at a rapid rate. Metals that are soft and readily damaged or worn mechanically, such as copper and lead, are quite susceptible to erosion-corrosion. Factors influencing erosion corrosion are discussed below

2.11.1 Surface Films

The nature and properties of the protective films that form on some metals or alloys are very important from the standpoint of resistance to erosion-corrosion. A hard, dense adherent and continuous film would provide better protection than one that is easily removed by mechanical means or worn off. A brittle film that cracks or breaks up under stress may not be protective.

2.11.2 Effect of Velocity

The velocity of the environment plays an important role in erosion-corrosion Table 2.2 shows the effect of velocity on a variety of materials and alloys exposed to seawater. These data show that the effect of velocity can range from nil to extremely great.

Increases in velocity result in increased attack, particularly if substantial rates of flow are involved. Table I.2 lists several examples exhibiting little effect when the velocity is increased from 30-120 cm/sec but destructive attack will be at 820 cm/sec. This high velocity is below the critical value for other materials listed at the bottom of the table.

2.11.3 Effect of Turbulent Flow

Many erosion-corrosion failures occur because turbulent flow conditions exist. This type of failure occurs in the inlet ends of tubing in condensers and similar shell-and-tube heat exchangers and is designated “inlet-tube corrosion.”

2.11.4 Effect of Impingement

Many failures are directly attributed to impingement. The vertical and horizontal runs of pipe were unaffected, but the metal failed where water was forced to turn its direction of flow.

2.11.5 Galvanic Effect

Galvanic or two-metal corrosion can influence erosion-corrosion when dissimilar metals are in contact in a flowing system.

2.11.6 Nature of Metal or Alloy

The chemical composition, corrosion resistance, hardness, and metallurgical history of metals and alloys can influence the performance of these materials under erosion-corrosion conditions.

Other forms of erosion-corrosion damages are cavitation damage and fretting corrosion. The first is caused by the formation and collapse of vapor bubbles in a liquid near a metal surface and the second is due to contact areas between materials under load subjected to vibration and slip. It appears as pits or grooves in the metal surrounded by corrosion products. Fretting is also called "friction oxidation," "wear oxidation," "chafing," and "false brinelling" (so named because the resulting pits are similar to the indentations made by a Brinell hardness test).

2.11.7 Combating Erosion-Corrosion

Five methods for prevention or minimization of damage due to erosion-corrosion are used. In order of importance they are:

- Materials with better resistance to erosion corrosion
- Design
- Alteration of the environment
- Coatings
- Cathodic protection.

2.12 Stress Corrosion Cracking

Stress corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium.

Many investigators have classified all cracking failures occurring in corrosive mediums as stress-corrosion cracking, including failures due to hydrogen embrittlement. These two types of cracking failures respond differently to environmental variables. To illustrate, cathodic protection is an effective method for preventing stress-corrosion cracking whereas it rapidly accelerates hydrogen-embrittlement effects. Hence the importance of considering stress-corrosion cracking and hydrogen embrittlement as separate phenomena is obvious.

During stress-corrosion cracking, the metal or alloy is virtually unattached over most of its surfaces while fine cracks progress through it. This is illustrated in Figure 2.19.

Cross sections of SCC frequently show branched cracks. This river branching pattern is unique to SCC and is used in failure analysis to identify when this form of corrosion has occurred.

This cracking phenomenon has serious consequences since it can occur at stresses within the range of a typical design.

The two classic cases of stress-corrosion cracking are the "season cracking" of brass, and the "caustic embrittlement" of steel. Both of these obsolete terms describe the environmental conditions

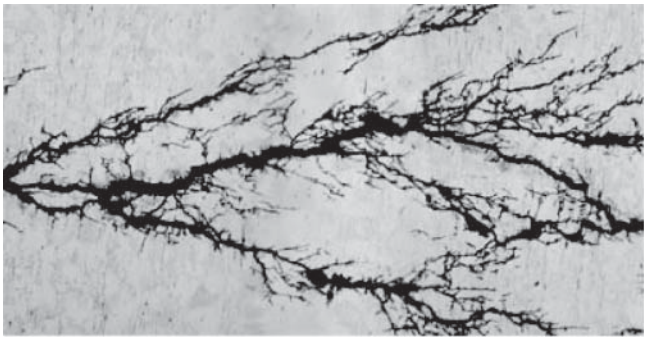


Figure 2.19 *Branched cracks in stress-corrosion cracking. (Reproduced with permission from Daubert Cromwell.)*

present that led to stress-corrosion cracking. While the effects of stress alone are well known in mechanical metallurgy (i.e., creep, fatigue, tensile failure) and corrosion alone produces characteristic dissolution reactions, the simultaneous action of both sometimes produces disastrous results.

2.12.1 Crack Morphology

Intergranular and transgranular stress-corrosion cracking are observed. Intergranular cracking proceeds along grain boundaries, while transgranular cracking advances without apparent preference for boundaries.

2.12.2 Stress Effects

Increasing the stress decreases the time before cracking occurs. There is some conjecture concerning the minimum stress required to prevent cracking. This minimum stress depends on temperature, alloy composition, and environment composition. In some cases it has been observed to be as low as about 10% of the yield stress. In other cases, cracking does not occur below about 70% of the yield stress. For each alloy environment combination there is probably an effective minimum or threshold stress. This threshold value must be used with considerable caution since environmental conditions may change during operation.

2.12.3 Corrosion Fatigue

Fatigue is defined as a tendency of a metal to fracture under repeated cyclic stressing. Usually fatigue failures occur at stress levels below the yield point and after many cyclic application of this stress.

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment. Damage from corrosion fatigue is greater than the sum of the damage from both cyclic stresses and corrosion. Control of corrosion fatigue can be accomplished by either lowering the cyclic stresses or by corrosion control.

2.12.4 Methods of Prevention

The mechanism of stress-corrosion cracking is imperfectly understood. Prevention methods are either general or empirical in nature. Stress-corrosion cracking may be reduced or prevented by application of one or more of the following methods:

- Lowering the stress below the threshold value if one exists.
- Eliminating the critical environmental species by degasification, demineralization, or distillation.
- Changing the alloy, if neither the environment nor stress can be changed.
- Applying cathodic protection to the structure with an external power supply or consumable anodes.
- Adding inhibitors to the system if feasible.
- Coatings are sometimes used, and they depend on keeping the environment away from the metal, for example coating vessels and pipes that are covered with insulation.
- Shot peening (also known as shot blasting), produces residual compressive stresses in the surface of the metal.

2.13 Types of Hydrogen Damage

Hydrogen damage though not a form of corrosion, often occurs indirectly as a result of corrosive attack and therefore it is included in this form of corrosion and is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with hydrogen. It is classified into four distinct types:

- Hydrogen blistering (Figure 2.20)
- Hydrogen embrittlement
- Decarburization
- Hydrogen attack.

Hydrogen damage may be defined as reduction of the load-carrying capacity by the admission of hydrogen into the metal.

2.13.1 Causes of Hydrogen Damage

Hydrogen damage is the mechanical damage of a metal caused by the presence of, or interaction with, hydrogen. Hydrogen blistering and hydrogen embrittlement are caused by penetration of atomic hydrogen into the metal. Decarburization is caused by moist hydrogen at high temperatures. Hydrogen attack is a disintegration of oxygen-containing metal in the presence of hydrogen. The origin of the hydrogen can be found in cleaning, pickling, cathodic protection, welding, treatment, and operation.

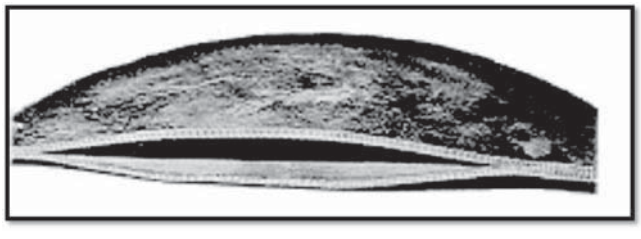


Figure 2.20 *Typical hydrogen blistering. (Reproduced with permission from Analog © Luis Orozco.)*

2.13.2 Preventive Measures

- Select a clean metal.
- Select a resistant material, homogenous or clad.
- Select low-hydrogen welding electrodes and specify welding in dry conditions.
- Select correct surface preparation and treatment.
- Avoid incorrect pickling and plating procedures.
- Metalize with resistant metal, or use a clad metal.
- Induce compressive stresses.

2.14 Concentration Cell Corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. There are three general types of concentration cell corrosion:

- Metal ion concentration cells
- Oxygen concentration cells
- Active–passive cells.

2.14.1 Metal Ion Concentration Cells

In the presence of water, a high concentration of metal ions will exist under faying surfaces and a low concentration of metal ions will exist adjacent to the crevice created by the faying surfaces. An electrical potential will exist between the two points. The area of the metal in contact with the low concentration of metal ions will be cathodic and will be protected, and the area of metal in contact with the high metal ion concentration will be anodic and corroded. This condition can be eliminated by sealing the faying surfaces in such a manner as to exclude moisture. Proper protective coating application with inorganic zinc primers is also effective in reducing faying surface corrosion.

2.14.2 Oxygen Concentration Cells

A water solution in contact with the metal surface will normally contain dissolved oxygen. An oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse uniformly into the solution, thereby creating a difference in oxygen concentration between two points. Typical locations of oxygen concentration cells are under either metallic or non-metallic deposits (dirt) on the metal surface and under faying surfaces such as riveted lap joints. Oxygen cells can also develop under gaskets, wood, rubber, plastic tape, and other materials in contact with the metal surface. Corrosion will occur at the area of low oxygen concentration (anode). The severity of corrosion due to these conditions can be minimized by sealing, maintaining clean surfaces, and avoiding the use of material that permits wicking of moisture between faying surfaces.

2.14.3 Active–Passive Cells

Metals that depend on a tightly adhering passive film (usually an oxide) for corrosion protection, e.g., austenitic corrosion-resistant steel, can be corroded by active–passive cells. The corrosive action usually starts as an oxygen concentration cell, e.g., salt deposits on the metal surface in the presence



Figure 2.21 *"Worm-like" filiform corrosion tunnels. (Reproduced with permission from Daubert Cromwell.)*

of water containing oxygen can create the oxygen cell. If the passive film is broken beneath the salt deposit, the active metal beneath the film will be exposed to corrosive attack. An electrical potential will develop between the large area of the cathode (passive film) and the small area of the anode (active metal). Rapid pitting of the active metal will result. This type of corrosion can be avoided by frequent cleaning and by application of protective coatings.

2.15 Filiform Corrosion

This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating. Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided unless the absence of an adverse effect has been proven by field experience. Where a coating is required, it should exhibit low water vapor transmission characteristics and excellent adhesion. Zinc-rich coatings should also be considered for coating carbon steel because of their cathodic protection quality.

Figure 2.21 shows "worm-like" filiform corrosion tunnels forming under a coating at the Atmospheric Test Site.

2.16 Types of Intergranular Corrosion

Intergranular corrosion is an attack on or adjacent to the grain boundaries of a metal or alloy. A highly magnified cross section of most commercial alloys will show its granular structure. This structure consists of quantities of individual grains, and each of these tiny grains has a clearly defined boundary that chemically differs from the metal within the grain center. Heat treatment of stainless steels and aluminum alloys accentuates this problem.

Figure 2.22 shows a stainless steel that corroded in the heat-affected zone a short distance from the weld. This is typical of intergranular corrosion in austenitic stainless steels. This corrosion can be

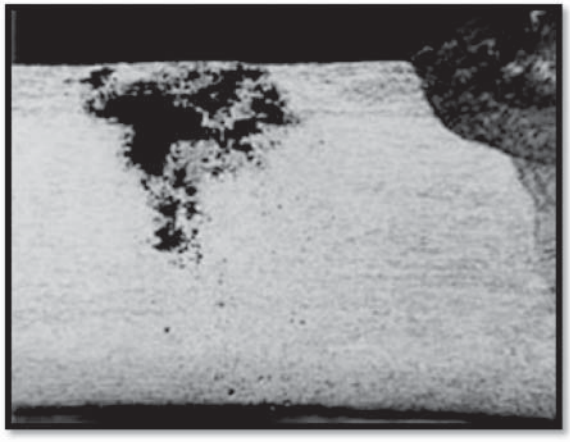


Figure 2.22 *A stainless steel that corroded in the heat-affected zone a short distance from the weld. (Reproduced with permission from Daubert Cromwell.)*

eliminated by using stabilized stainless steels (321 or 347) or by using low-carbon stainless grades (304L or 3I6L).

2.17 Microbiologically Influenced Corrosion

Microbial corrosion (also called microbiologically influenced corrosion or MIC) is corrosion that is caused by the presence and activities of microbes. This corrosion can take many forms and can be controlled by biocides or by conventional corrosion control methods.

There are a number of mechanisms associated with this form of corrosion, and detailed explanations are available in the literature. Most MIC takes the form of pits that form underneath colonies of living organic matter and mineral and biodeposits. This biofilm creates a protective environment where conditions can become quite corrosive and corrosion is accelerated.



Figure 2.23 *The combination of rust and organic debris. (Reproduced with permission from Daubert Cromwell.)*

MIC can be a serious problem in stagnant water systems such as those used for fire protection. The use of biocides and mechanical cleaning methods can reduce MIC, but anywhere where stagnant water is likely to collect is a location where MIC can occur. Corrosion (oxidation of metal) can only occur if some other chemical is present to be reduced.

In most environments, the chemical that is reduced is either dissolved oxygen or hydrogen ions in acids. In anaerobic conditions (no oxygen or air present), some bacteria (anaerobic bacteria) can thrive. These bacteria can provide the reducible chemicals that allow corrosion to occur. That is how the limited corrosion that was found on the hull of Titanic occurred. Figure 2.23 shows a "rusticle" removed from the hull of Titanic. This combination of rust and organic debris clearly shows the location of rivet holes and where two steel plates overlapped.

2.18 Corrosion in Concrete

Figure 2.24 shows cracking and staining of a seawall.

Concrete is a widely used structural material that is frequently reinforced with carbon steel reinforcing rods, post-tensioning cable or prestressing wires. The steel is necessary to maintain the strength of the structure, but it is subject to corrosion. The cracking associated with corrosion in concrete is a major concern in areas with marine environments and in areas which use deicing salts.

There are two theories on how corrosion in concrete occurs:

1. Salts and other chemicals enter the concrete and cause corrosion. Corrosion of the metal leads to expansive forces that cause cracking of the concrete structure.
2. Cracks in the concrete allow moisture and salts to reach the metal surface and cause corrosion.



Figure 2.24 *Cracking and staining of a seawall. (Reproduced with permission from Daubert Cromwell.)*

Both possibilities have their advocates, and it is also possible that corrosion in concrete can occur either way. The mechanism isn't truly important, the corrosion leads to damage, and the damage must be controlled.

In new construction, corrosion in concrete is usually controlled by embedding the steel deep enough so that chemicals from the surface don't reach the steel (adequate depth of cover). Other controls include keeping the water/cement ratio below 0.4, having a high cement factor, proper detailing to prevent cracking and ponding, and the use of chemical admixtures. These methods are very effective, and most concrete structures, even in marine environments, do not corrode.

Unfortunately, some concrete structures do corrode. When this happens, remedial action can include repairing the cracked and spalled concrete, coating the surface to prevent further entry of corrosive chemicals into the structure, and cathodic protection, an electrical means of corrosion control.

3

Corrosion Considerations in Material Selection

Corrosion is the largest single cause of plant and equipment breakdown in the oil, gas, and chemical processing industries. For most applications it is possible to select materials of construction that are completely resistant to attack by the process fluids, but the cost of such an approach is often prohibitive. In practice it is usual to select materials that corrode slowly at a known rate and to make an allowance for this in specifying the material thickness. Moreover, it is important to take into account that external atmospheric corrosion leads to many instances of loss of containment and tends to be a greater problem than internal corrosion. All these aspects of corrosive behavior need to be addressed, both at the plant design stage and during the life of the plant.

3.1 Corrosion in Oil and Gas Products

Corrosion has been widely experienced in the oil and gas industry. In the following, the main corrosion processes in oil and gas phases are discussed.

First of all it must be emphasized that corrosion is likely to occur only in the water phase, as the oil phase is considered non-corrosive. Consequently, the presence of free water is necessary for corrosion to occur, i.e. vaporized water in streams at temperatures above the dew point are considered non-corrosive.

In addition, it is necessary, especially for mixed phase streams (oil + gas + water) to verify the water wetting of materials, in fact, if water is confined in the middle of the stream, or trapped by oil, no corrosion attack may develop. The principle factors controlling corrosion are:

- the CO_2 partial pressure
- the H_2S partial pressure
- the fluid temperature
- the water salinity
- the water cut

Corrosion and Materials Selection: A Guide for the Chemical and Petroleum Industries, First Edition. Alireza Bahadori.
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- the fluodynamics
- the pH.

Additional factors influencing corrosion rates in petroleum refineries and petrochemical plants including offsite facilities and pollution control facilities are:

- organic acids (naphthenic acids)
- hydrogen (atomic)
- amine solution
- sulfur
- sodium hydroxide
- ammonia
- hydrofluoric acid
- glycol
- cyanide
- sulfuric acid
- galvanic couple
- stress (plus chlorides, caustic, ammonia, amines, polythionic acid)
- bacteria
- concentration of corrosives
- aeration
- heat flux
- welding defects
- high-temperature oxidation and corrosion.

3.1.1 Effect of CO_2

Dry CO_2 is non-corrosive up to about 400 °C, while it is corrosive when dissolved in water. CO_2 corrosion in the presence of free water is known as sweet corrosion. CO_2 dissolves in the water phase forming carbonic acid, which decreases the water acidity; the final pH of the solution will depend on the temperature and CO_2 partial pressure. The corrosivity of CO_2 saturated solutions is much higher than other acid solutions at the same pH, because of the direct action of CO_2 in the corrosion phenomena.

3.1.2 Effect of Temperature

Laboratory studies have shown that the corrosion rate increases up to 70 °C, probably due to the increase of mass transfer and charge transfer rates. Above this temperature, the corrosion rate starts to decrease. This fact is attributed to the formation of a more protective scale, due to a decrease in iron carbonate solubility, and consequently the diffusion process becomes the rate-determining step.

3.1.3 Effect of Pressure

The partial pressure of CO_2 affects the corrosion rate. Since it is proportional to the total pressure by $P_{CO_2} = P \times \text{mol\% } CO_2$, the corrosion rate will increase with increasing pressure.

3.1.4 Prediction of CO_2 Corrosion Rate

The corrosion rate of carbon steels in CO_2 -saturated water may be evaluated according to the de Waard and Milliams formula, where the corrosion rate is an exponential function of CO_2 partial

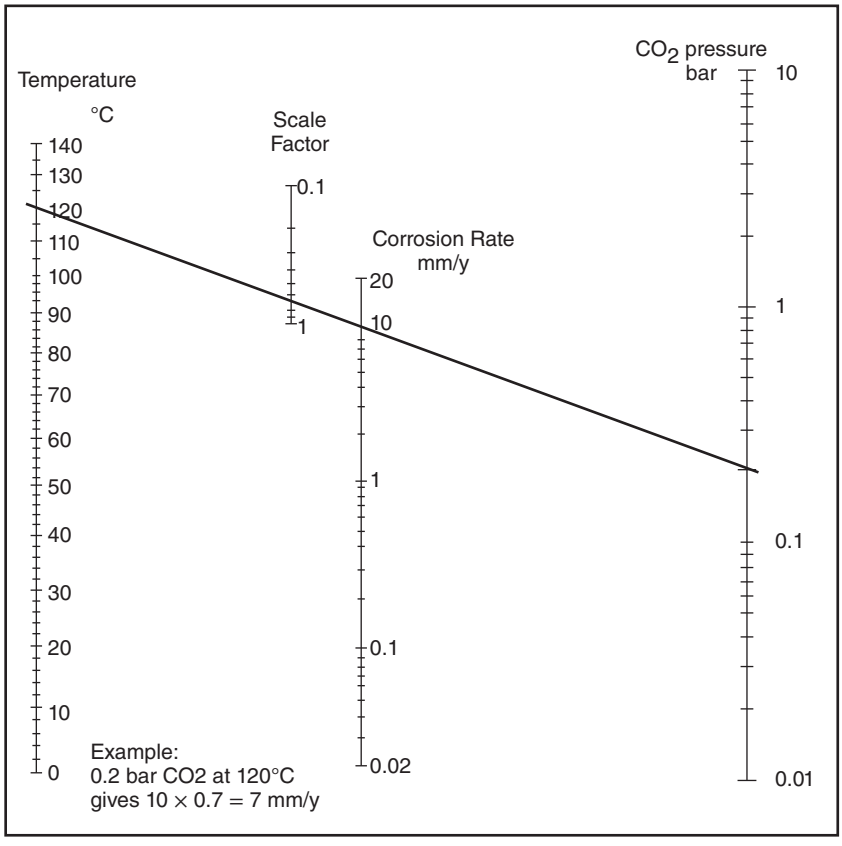


Figure 3.1 *de Waard and Milliams Nomogram. (Poling, B.E., Prausnitz, J.M., and O'Connell,* J.P: Properties of gases and liquids*, 5th Edition, McGraw Hill, 2002.)*

pressure and temperature. Results obtained following this approach should be considered worst case corrosion.

The formula is easily usable in the form of a nomogram (Figure 3.1).

$$\log(R_{\max}) = 5.8 - \frac{1710}{T} + 0.67\log(P_{CO_2}) \tag{3.1}$$

where:

$R_{\max}$ = corrosion rate (mm/yr)
T = temperature (K)
$P_{CO_2} = P.m_{CO_2}$

with P being the total pressure (bar) and m_{CO_2} the CO_2 molar fraction in the gas phase.

For high pressures, it is recommended to substitute the partial pressure with the fugacity, defined as:

$$f_{CO_2} = a.P_{CO_2} \tag{3.2}$$

with a being the activity coefficient, given by:

$$\log(a) = \left(0.0031 - \frac{1.4}{T}\right)P \tag{3.3}$$

The validity limits under which the above formula was originated are:

- $P_{CO_2} < 2$ bar
- Temperature $< 70°C$
- Water is distilled.

The fitness of this formula has also been confirmed for CO_2 partial pressures much higher than the original experimental work.

R_{max} may be adjusted by considering the influence of the rest of the environment, other than P_{CO_2} and T. The final corrosion rate may be thus expressed as:

$$R_{corr} = R_{max} \times F_g \times F_s \times F_w \times F_i \times F_c \times F_{pH} \tag{3.4}$$

where the following reduction factors are applicable:

3.1.4.1 *Effect of Glycol – F_g*

In wet CO_2-containing pipelines and flowlines, glycol is often injected to prevent hydrate formation. Glycols have a significant inhibitive effect on corrosion. The reduction of the expected corrosion rate due to the presence of triethylene glycol (TEG) can be conservatively expressed by F(g):

$$\log(F_g) = 1.6 \log W(g) - 3.2 \tag{3.5}$$

For mono and diethylene glycol the available data are more limited, but the results are also covered by the above F_g factor.

3.1.4.2 *Effect of Scaling – F_s*

At temperatures higher than about 70 °C, the steel may be protected by its corrosion products (iron carbonate, $FeCO_3$), and consequently the corrosion rate may be depressed, by a coefficient F_s representing the scaling factor:

$$\log(F_s) = \frac{2400}{T} - 0.6 \log(f_{CO_2}) - 6.7 \leq 1 \tag{3.6}$$

Between 70 and 150 °C, carbon steels are more prone to localized attack in cases of high turbulence, as a consequence of the failure of the $FeCO_3$ film. In this case, the corrosion rate may be much higher.

At temperatures higher than 150 °C and CO_2 partial pressures below 50 bar, the steel is protected by a strong film of $FeCO_3$ that is not removed, even by high turbulent streams, and the corrosion rate becomes negligible.

Corrosion morphology may be either uniform or localized (mesa or pitting), according to the process parameters (temperature, CO_2 partial pressure, water phase composition, flow rate).

3.1.4.3 *Effect of Water Cut – F_w*

Oil presence is generally considered beneficial, as far as oil exerts a kind of inhibition effect. In fact, on a steel surface, oil may form a film thick and adherent enough to inhibit water wetting. On the other hand, gas and condensates do not generally exert any beneficial effect, as they have no inhibition property.

Hydrocarbon condensates are assumed not to influence corrosion significantly. Field experience has shown that, as opposed to oil, the hydrophobic behavior of condensates is negligible. As far as vertical tubing is concerned, an oil film on the steel surface is stable up to about 20–40% water cuts. For higher water quantities the corrosion rate can be correctly predicted by the de Waard and Milliams equation, as the steel may be considered water wet.

As far as horizontal pipes are concerned, the amount of water is not an important factor. In fact, as water is generally heavier than oil, gas, and condensed products, in the case of stratified flow, it may separate onto the lowest surfaces, generally at the 6 o'clock position. In this case, the expected corrosion will occur only on the water wetted surfaces.

In the case of stratified flow, corrosion is also likely to occur at the top of the line, due to the condensation of water droplets from the wet gas. The effect of inhibition is poor in this case, and experience shows that corrosion rates at the top of the line can be assumed to be 10% of the predicted rate in fully immersed conditions, with a maximum of about 0.3 mm/yr, irrespective of the CO_2 content. To increase the inhibition efficiency in stratified flow, periodic pig launches should be made to allow an inhibitor film to form at the top of the line.

In these cases, corrosion attack will be localized at the 6 o'clock position, and, anyway, the rate may be correctly predicted with the approach discussed in this section. Pigging of the line is generally useful to remove any water remaining stagnant in the pipe.

This will also allow better inhibition of the pipe surfaces; if the inhibitors are oil-soluble products, they are transported by the oil phase, and inhibition in stagnant water may be difficult. When corrosion protection by inhibitors is of the utmost important, it is common practice to pig the lines regularly (daily or weekly).

In the case of higher gas flow rates, the flow pattern may become annular, for horizontal pipes, where a continuous liquid film (which varies in thickness around the circumference of the pipe) exists over the full pipe circumference, whilst gas flows in the middle of the pipe. Since the steel surface is completely wetted, corrosion is equally likely to occur at any point around the circumference. When using flow pattern diagrams, the superficial velocity may be defined as the velocity the (liquid/gas) phase would exhibit if it flowed through the total cross section of the pipe alone.

Protection in this case may be achieved through continuous injection of film-forming corrosion inhibitors, as they can be transported by the water phase and film over the full pipe surface. Attention should be paid in this case to the flow velocity, as highly turbulent flow may produce high shear stresses on the pipe wall and remove the inhibitor film.

Another important factor in this case is the avoidance (or reduction) of disturbances, like small-radius bends, over-penetrated root welds, or sudden changes of diameter or direction, as they could create turbulence and impingement after the discontinuities, remove the inhibitor film, and promote a high rate of corrosion. To conclude, for light hydrocarbon condensate, water wetting may occur at any velocity, thus F_w is always set equal to 1.

3.1.4.4 Effect of Corrosion Inhibitors – F_i

It has been common practice for many years to inject corrosion inhibitors into CO_2-containing production tubing and process streams carried by carbon steels. In some cases inhibitors have been injected into nominally dry gas lines as a second defence to back up the drying process in the event of misoperation.

In some other cases, inhibitors are applied as the first line of defence against corrosion in carbon steel lines carrying wet gas from satellite to central gathering facilities, where bulk drying can be carried out. Temperature drops can be considerable over such intrafield lines, so that condensation of water and hence corrosion will take place over the full internal pipe surface.

Corrosion inhibitors are chemicals that may be divided into a few categories. Among these, the most used class in horizontal flow lines/pipelines is the film-forming amine type.

In this case, the inhibitor is composed of a flat aromatic molecule (amine), which is polar and is attracted by the steel surface, and is able to establish some absorption link; the molecule has also a long aliphatic tail, which is oil soluble.

The effect of a film-forming inhibitor is thus to establish a first layer of flat molecules just on the steel surface, a second layer of aliphatic tails and a third layer of oil/condensates. Thus, water cannot reach the steel surface and promote corrosion.

The stability of this film is dependent on the chemistry and fluodynamics of the transported fluids, as they can remove the inhibitors from the steel surface, because of the chemical affinity between oil products and the aliphatic tail, or promote breaking of this film by impingement of water droplets.

The effect of velocity on corrosion inhibitor performance is to reduce film life and increase the concentration of inhibitor required to maintain protection. It is generally accepted to define the capacity of inhibitors to protect against corrosion using a parameter, called efficiency, defined as:

$$\text{inhibitor efficiency} = \frac{R_{\text{corr}}\ (\text{without inhibitors}) - R_{\text{corr}}\ (\text{with inhibitors})}{R_{\text{corr}}\ (\text{without inhibitors})} \tag{3.7}$$

and often used as a percentage. To give an example, if a system exhibits a 2 mm/yr corrosion rate without inhibitors and 0.2 mm/yr with inhibitor injection, the calculated efficiency is 90%.

Under ideal conditions for inhibitor application, an inhibitor efficiency of above 85% can be achieved when comparing the actual corrosion rate with that predicted by the de Waard–Milliams nomogram in Figure 3.1. However, an efficiency of 85% is dependent upon even distribution of the inhibitor over the whole circumference of the pipe wall, something unlikely to be achieved in flowlines transporting a mixture of liquid and gas. In addition, areas of extreme turbulence can appear in connection with disturbances, which reduce the level of protection that an inhibitor can provide. Such disturbances have been seen at flanges and at over-penetrations at welds, and may also occur in areas of growing corrosion damage.

Experimental data for all inhibitors tested under two flow conditions showed that corrosion rates increased as superficial gas velocity increased; inhibition efficiency above 95% in single-phase flow decreased significantly in the range 40–95%, highlighting the necessity of qualifying the chemicals before injection through properly designed corrosion testing.

The persistence of the inhibitor film on steel surfaces depends on the inhibitor type and dosage. Moreover, it was found that the capacity of an inhibitor to produce resistant films is also dependent on the pH of the environment. Moreover, it was shown that increasing inhibitor concentration is usually required when high flow rate (i.e. high shear stresses) is expected.

Most inhibitors exhibit a maximum temperature, above which they do not function properly. Generally, it is believed that inhibitors in pipelines can work up to about 90 °C. For a given oil-soluble inhibitor, the parameters of primary importance that control corrosion rates in inhibited systems include inhibitor concentration, dispersion of inhibitor in water, film persistence, and velocity.

Parameters of secondary importance in predicting corrosion in inhibited wet gas pipeline include partial pressure of CO_2, temperature (if below a critical level), and composition of the aqueous environment (including pH). In other words, if the local concentration of an appropriate inhibitor is sufficiently high, corrosion may be controlled regardless of CO_2 partial pressure, fluid composition, or temperature in the range normally found in pipelines.

With this last approach, instead of calculating the expected corrosion rate or inhibitor efficiency, the reliability of corrosion inhibitors is the most important to define. To conclude, inhibitor efficiency is very difficult to establish, being dependent on:

- proper inhibitor selection and dosage,
- fluid velocity and flow regime,
- presence of disturbances able to preturbate the flow,
- operating temperature, in order to ensure persistence of the inhibitor film.

It is general practice, at the design stage, to assume an inhibitor efficiency of 0.9 (more precisely this figure should be 0.85 for condensate, 0.9 for gas, and 0.95 for oil streams), thus $F_i = 0.1$. However, lower figures should be considered where high flow velocities are expected to produce erosion-corrosion attacks in the presence of disturbances. In fact, it is possible to have erosive liquid flow at local flow disturbances such as weld beads, pin ends in connections, bends, size reduction,

and flanges, even where the bulk liquid flow rate is not high. For all these cases, the capacity and cost of field repair should become the effective design criteria.

3.1.4.5 *Effect of Condensing Phase – F_c*

In the case of water condensation from saturated vapor as a consequence of the stream cooling along the route of piping, corrosion is likely to occur under the condensed droplets. These conditions are very likely to produce a protective film, as scale deposition and adherence are favored because of the quiescent conditions. In fact, experiments and experience demonstrated that, in spite of the nomogram predicting the same value in immersed and condensing conditions, the corrosion rate drops at a maximum of 0.3 mm/yr, irrespective of the partial pressure of CO_2.

A similar reduction in the corrosion rate may be applied to reduce the expected corrosion rate for the top surface of vessels and separators etc. It is also applicable to the tops of pipelines where the flow regime is stratified, or nominally dry gas lines where cooling below the dew point occurs. No reduction is applicable to immersed conditions. Such a reduction factor may be evaluated as:

$$F_c = 0.4 \text{ (condensing rate, } g/(m^2.s)) \leq 1 \tag{3.8}$$

In most cases, the adoption of $F_c = 0.1$ is suggested, where applicable.

3.1.4.6 *Effect of Water Salinity – F_{pH}*

Corrosion in production fluids is mainly controlled by the presence of free water, which may come from the reservoir itself (formation water) and/or condense along the route (condensation water). These two types of water differ very much with regard to composition and their effect on corrosion phenomena.

In fact, whereas condensate free of salts can achieve very low pH, salts dissolved in formation water may have a buffering effect, leading to higher pH at the same CO_2 partial pressures. The solution pH will depend, finally, on the amount and kind of dissolved solids, and the dissolved gases.

In addition, the presence of ions (like Ca^{2+}, $Mg^{2+)}$ can increase the resistance of the corrosion product film, where the corrosion resistance may be influenced by this phenomenon. To evaluate F_{pH}, the saturation pH must be first calculated as the lowest of:

$$pH_{sat} = 1.36 + \frac{1307}{T} - 0.17 \log(f_{CO_2}) \tag{3.9}$$

which refers to the formation of Fe_3O_4 and

$$pH_{sat} = 5.4 - 0.66 \log(f_{CO_2}) \tag{3.10}$$

which refers to the formation of $FeCO_3$. Once the real environmental pH, pH_{act}, is known, the corrective factor F_{pH} may be calculated as:

$$\text{if} \quad pH_{sat} \geq pH_{act}$$

$$\log(F_{pH}) = 0.32(pH_{sat} - pH_{act}) \tag{3.11}$$

$$\text{if} \quad pH_{sat} \leq pH_{act}$$

$$\log(F_{pH}) = -0.13(pH_{sat} - pH_{act})^{1.6} \tag{3.12}$$

The adoption of such a reduction factor is not allowed if F_s is also used, thus F_{pH} is set to 1 if F_s is lower than 1. If the real environmental pH is unknown, F_{pH} is set at 1.

3.1.5 Effect of H_2S

H_2S in presence of water is known to cause sour corrosion. This name covers different mechanisms: uniform corrosion, sulfide stress cracking (SSC) and hydrogen induced cracking (HIC).

3.1.5.1 Uniform Corrosion

H_2S is a weak acid, so it causes a small decrease in the pH of the water solution. Nevertheless, it may also corrode in neutral solutions, with a uniform corrosion rate generally quite low, as shown in Figures 3.2 and 3.3.

Furthermore, H_2S may play an important role in the mechanical resistance of corrosion product films, increasing or decreasing their strength, depending on the relative amount, as shown in Figure 3.4.

3.1.5.2 Hydrogen-induced cracking

This form of attack, also known as stepwise cracking, is typical of carbon steels showing ferritic structures, when in the presence of MnS (Type II) elongated inclusions as a consequence of rolling manufacturing processes.

Hydrogen-induced cracking (HIC) can occur in susceptible steels exposed to aqueous environments containing hydrogen sulfides. It is a form of hydrogen-related cracking and can have two distinct morphologies:

1. The first type is commonly referred to as HIC and can occur where little or no applied or residual tensile stress exists. It manifests as blisters or blister cracks oriented parallel to the plate surface.
2. The second type produces an array of blister cracks linked together in the through thickness direction by transgranular cleavage cracks. This type of cracking is referred to as stress-oriented hydrogen-induced cracking (SOHIC) and can have a greater effect on serviceability than HIC because it effectively reduces load carrying capabilities to a greater degree.

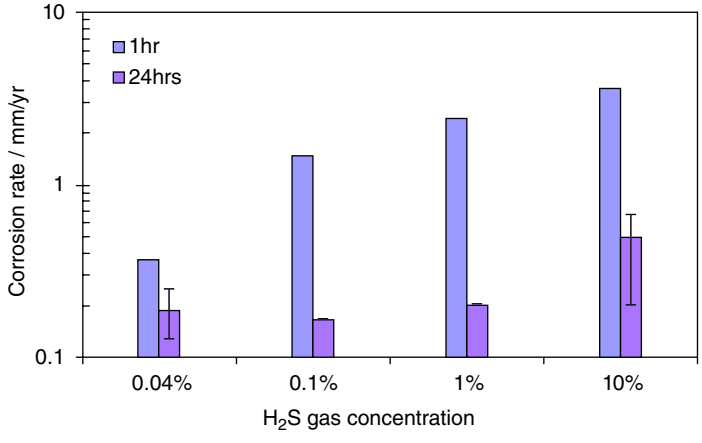


Figure 3.2 *The corrosion rate versus H_2S gas concentration after 1 h and 24 h exposure at total pressure $P = 1$ bar, $T = 80$ °C, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0–5.5. (Wei Sun and Srdjan Nesic; A mechanistic model of H_2S corrosion of mild steel; 2007, paper number 07655, NACE International Conference and Exhibition.)*

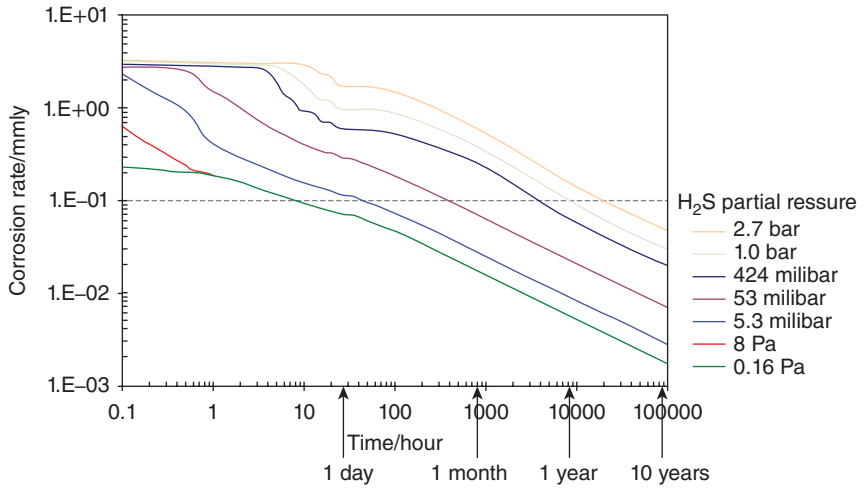


Figure 3.3 *Simulated corrosion rate as a function of time for a range of H_2S partial pressures; conditions: T = 80 °C, pH 5, and stagnant. (Wei Sun and Srdjan Nesic; A mechanistic model of H_2S corrosion of mild steel; 2007, paper number 07655, NACE International Conference and Exhibition.)*

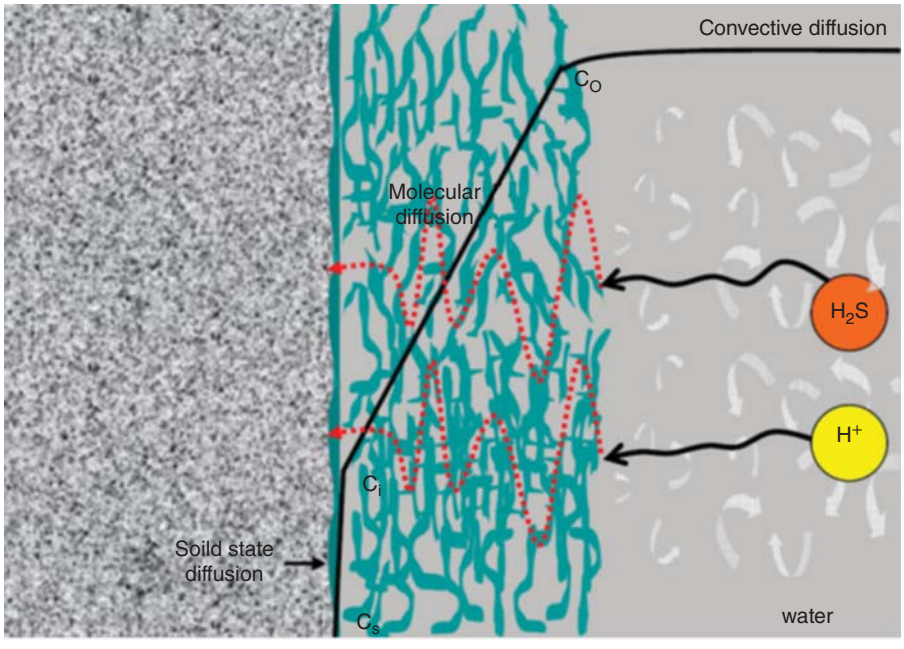


Figure 3.4 *A schematic of the H_2S corrosion process. (Wei Sun and Srdjan Nesic; A mechanistic model of H_2S corrosion of mild steel; 2007, paper number 07655, NACE International Conference and Exhibition.)*

Particularly common in the oil and gas industry, where the use of steel pressure vessels is widespread, the risks of HIC should be considered when hydrogen sulfide partial pressure becomes greater than 3.5 mbar. Carbon steel pressure vessels should not be affected by HIC damage where H_2S levels are lower than this figure in a normal service life cycle. HIC is prevalent in wet H_2S environments, which is often known as sour service; such cracking over a prolonged period of time without inspection will reach a critical point and the steel component, i.e. pressure vessel, could easily fail.

Simply put, HIC damage increases as the level of hydrogen sulfide increases.

At operating temperatures higher than 65 °C the risk of HIC is very low, and precautions against HIC damage are generally unnecessary. This kind of attack must be avoided through proper selection of carbon steel chemical analysis and corrosion resistance verified through testing during manufacturing. Figure 3.5 shows an example of hydrogen-induced cracking.

3.1.5.3 Sulfide Stress Cracking

This kind of attack occurs under the combined action of tension stresses and an aggressive environment (H_2S) when in presence of a susceptible material.

Sulfide stress cracking affects high strength carbon steels, especially in petroleum production and petroleum refining. SSCC is a specialized case of hydrogen cracking as it may be possible that sulfide stress corrosion cracking and hydrogen cracking proceed simultaneously.

The mechanism is as follows:

Iron is oxidized to the ferrous form at the anode and hydrogen sulfide undergoes a two-step dissociation at the cathode as shown below.

$$\text{At the anode} \rightarrow Fe \leftrightarrow Fe^{2+} + 2e \tag{3.13}$$

$$\text{At the cathode} \rightarrow H_2S + H_2O \leftrightarrow H^+ + HS^- + H_2O \tag{3.14}$$

$$HS^- + H_2O \leftrightarrow H^+ + S^- + H_2O \tag{3.15}$$

$$\text{Production combination} \rightarrow 2e + 2H^+ + Fe^{2+} + S^- \leftrightarrow 2H^0 + FeS \text{ (trolite)} \tag{3.16}$$

$$\text{The net reaction is} \rightarrow Fe + H_2S \leftrightarrow FeS + 2H^0 \tag{3.17}$$

As shown by the above reaction, not only is FeS formed, but other sulfides such as FeS_2 (pyrite), Fe_7S_8 (pyrrhotite) and Fe_9S_8 (kansite) may also be produced. At low H_2S pressures (0.0009 to 0.1 psi)



Figure 3.5 *Hydrogen-induced cracking. (Reproduced with permission from Daubert Cromwell.)*

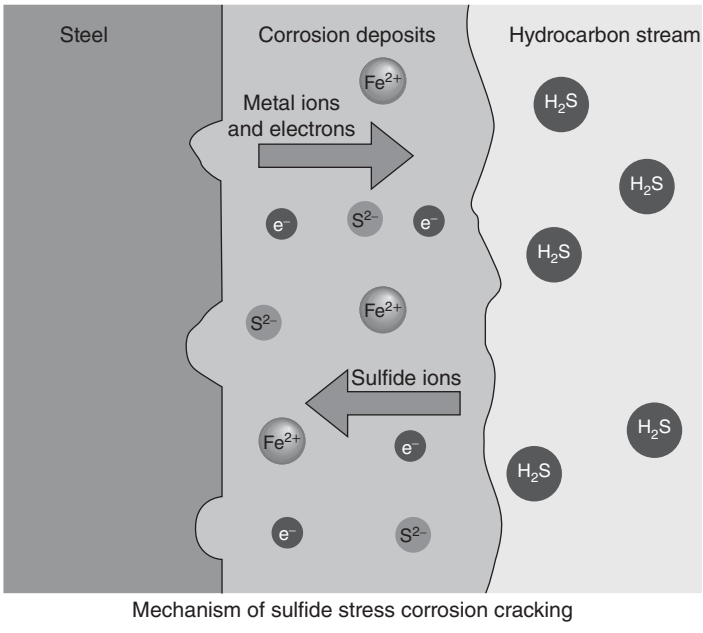


Figure 3.6 *Mechanism of sulfide stress corrosion cracking.*

the sulfide film is generally made up of pyrite, trolite, and some kansite and a lower rate of corrosion is observed. Increasing concentration of kansite leads to an increase in the corrosion rate. Figure 3.6 shows the typical mechanism of sulfide stress corrosion cracking.

Other factors affecting SSCC:

- SSCC may occur if the partial pressure of H_2S exceeds 0.01 atm for a 130 ksi yield strength steel.
- pH: lower pH adversely affects SSCC.
- Chlorides: SSCC is accelerated by chlorides in 12% chromium steel but the effect is not significant in low alloy steels.
- Temperation: SSCC occurs predominantly about 20%
- Hardness: the susceptibility to SSCC increases with increased strength. Steels with HRC over 22 are especially susceptible to SSCC.
- Cold working: this decreases the resistance to SSCC due to increasing residual tensile stress.

Examples of chloride-induced SCC are shown in Figure 3.7 below. The samples are taken from a pump transporting hydrocarbons.

3.1.5.4 Effect of Fluodynamics

Fluodynamics exerts an important influence on the corrosion rate. When increasing the flow rate, the primary effect is a higher mass transfer from the bulk of the solution to the near metal surface, which enhances both the corroding species and the mobility of the corrosion products. Higher flow rate produces higher corrosion rates.

The dependence of the corrosion rate on liquid flow velocity decreases with increased pH. This is important for practical situations, where dissolved $FeCO_3$ can increase the pH significantly. It is recommended to determine an approximate pH of the water phase for various conditions (see Figures 3.8 and 3.9).

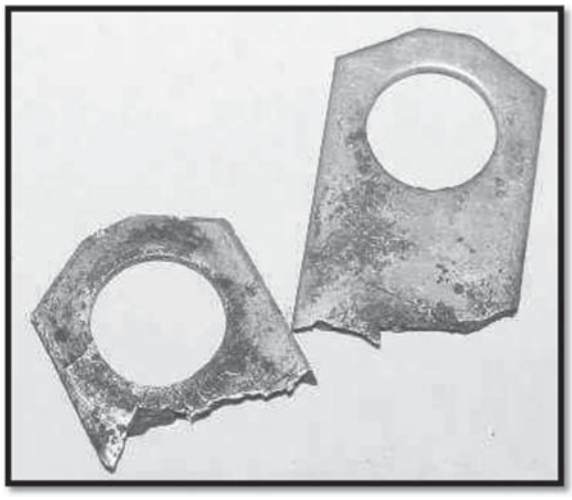


Figure 3.7 *A sleeve showing signs of chloride-induced stress corrosion cracking. The crack is at right angles to the retaining screw point which is the point of maximum stress.*

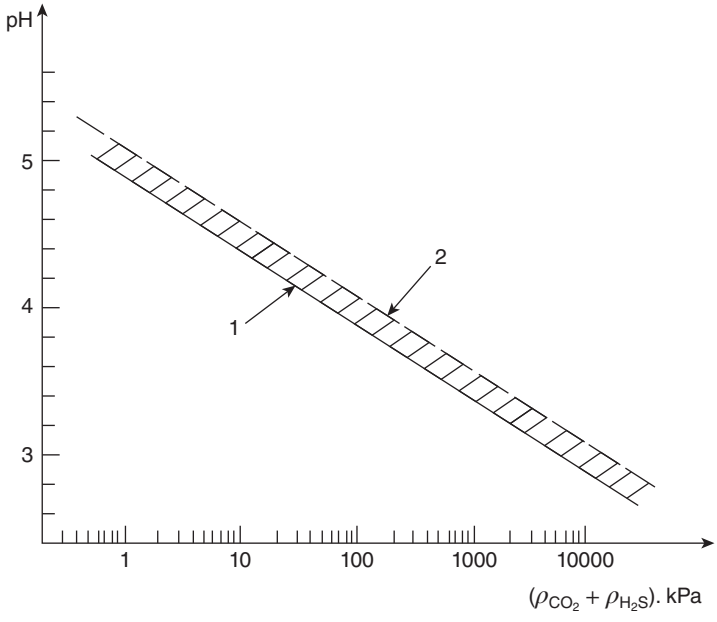


Figure 3.8 *The pH of condensed water under CO_2 and H_2S pressure. 1 : T = 20 °C;2 : T = 100 °C.*

The dependence of the corrosion rate on liquid flow velocity decreases with increasing pH, as demonstrated in Figure 3.10 This is important for practical situations, where dissolved $FeCO_3$ can increase the pH significantly.

The effect of velocity on the corrosion rate of steels is also dependent on steel composition and microstructures. Steels with more homogeneously distributed carbides as in tempered martensite

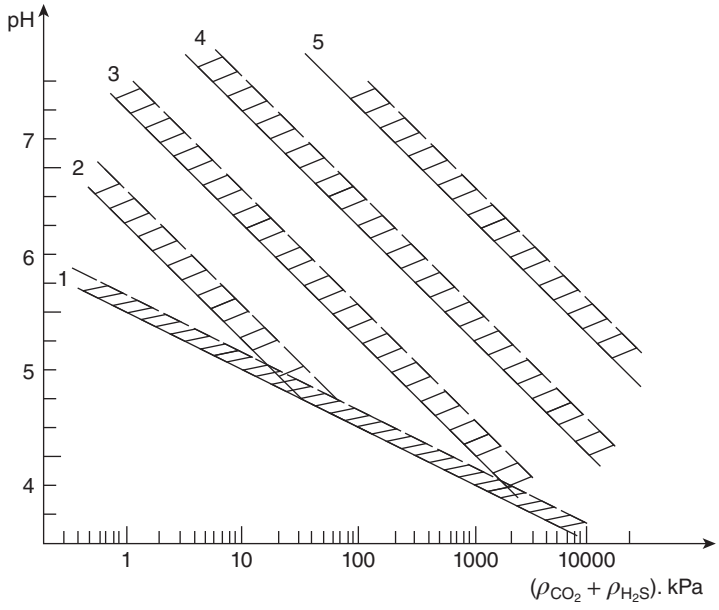


Figure 3.9 *The pH of condensate water (wet gas) or formation waters containing bicarbonate (undersaturated in $CaCO_3$) under CO_2 and H_2S pressure.*

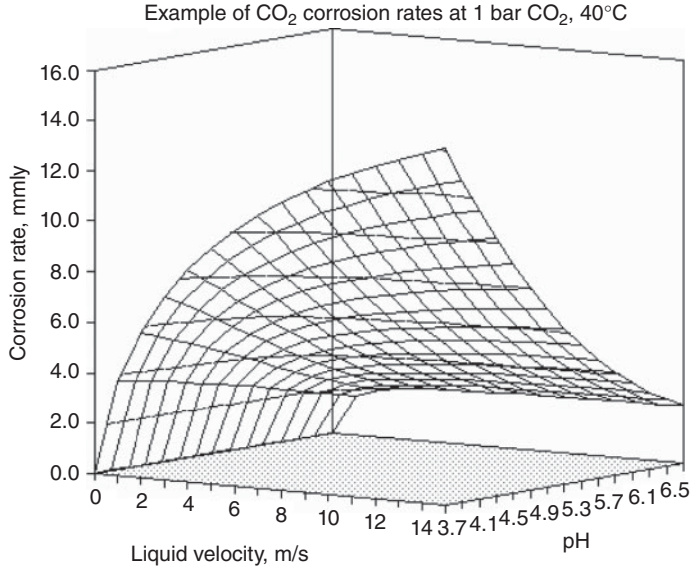


Figure 3.10 *The dependence of the corrosion rate on liquid flow velocity.*

and in bainitic structures are not expected to form lamellar cementite, which can act as a cathodic depolarizer and stimulator of CO_2 corrosion. Also, the effect of Cr appears to be a partial blockage of the surface, probably by chromium oxide, which interferes with the corrosion reaction.

The differences in the baselines with Cr% = 0 or C% = 0 indicates that martensitic steels could corrode somewhat faster than normalized ones. When the flow rate produces friction stresses on the corrosion product (or inhibitor) film, it may break them, with the result of a much higher corrosion rate. Conversely, as with horizontal pipes, low flow rates are generally not able to remove the free water that is stagnant at the 6 o'clock position.

When the flow rate is high, it is possible that corrosion product or inhibitor protective films are removed, giving a high chance corrosion occurring. This kind of attack is also called erosion-corrosion. API RP-14E/15/ contains a simple formula for estimating the velocity beyond which accelerated corrosion due to erosion corrosion may occur. The formula is empirical and derived from field experiences, and is meant to describe the velocity of the possible onset of erosion-corrosion in uninhibited corrosive oil- and gas-well surface production equipment fabricated from carbon steel in the absence of sand:

$$V = \frac{122}{\sqrt{\rho}} \tag{3.18}$$

where:

V = velocity beyond which accelerated corrosion may occur (m/s)

ρ = fluid density (kg/m^3).

Several authors have observed that erosion-corrosion happens in annular mist regimes. It is also indicated that the increase in corrosion rate with velocity in the Khuff Gas sour production system was associated with the onset of an annular mist regime in multi-phase flow. Here, without inhibitor injection, the corrosion rate dramatically increased at about 5 m/s flow rate; with inhibitor injection, on straight sections, this change happened at about 7–8 m/s. Of course these figures are strictly valid for the Khuff Gas experience only, and cannot be extrapolated to other conditions. From this experience, the following general rules can be derived:

- The calculated API erosional velocity is associated with the onset of annular mist flow.
- The onset of erosion-corrosion in uninhibited systems is associated with the onset of an annular mist flow regime in multi-phase flow in the surface piping.
- The onset of erosion-corrosion in inhibited systems (straight portions) occurs at a velocity of about 1.5 times the calculated API erosional velocity.

3.2 Corrosives and Corrosion Problems in Refineries and Petrochemical Plants

The following are the main corrosives and corrosion problems, in addition to those explained in previous sections, that require special material consideration in petroleum refineries and petrochemical plants.

3.2.1 Sulfur Content

Organic sulfur-bearing fluids ($\geq$ r 0.1 wt%) corrode steel at high temperature. Based on accumulated experience in actual plant design. Chromium-molybdenum steel is normally employed instead of carbon steel for the parts, where the operating temperature requires it.

3.2.2 Erosion

A serious erosion problem may arise around HDS piping and effluent air coolers downstream of the water injection point. Materials and fluid velocity should be determined by R.L. Piehls method.

3.2.3 Naphthenic Acid

Crude oil with an acidic value exceeding 0.5 mg KOH/g may pose serious corrosion problems for heater tubes, piping, and rotary machines. Austenitic stainless steel of 316 grade should be selected for parts handling high-temperature (over 260 °C) crude oil having high acidity.

3.2.4 Hydrogen

High-temperature and -pressure sections are subject to hydrogen attack. Materials for such services should be selected using the curves in the latest edition of API. This should also be considered for equipment located downstream of the waste heat boiler.

3.2.5 Polythionic Stress Cracking

Normal 304 stainless steel becomes subject to polythionic stress corrosion cracking because it sensitizes after welding and/or long-term exposure under high-temperature service. To avoid sensitization, stabilized austenitic stainless steel such as Type 321 or 347 may be selected.

3.2.6 Caustic Embrittlement by Amine Solution

Piping and equipment in direct contact with amine solution should be stress relieved to avoid caustic embrittlement, provided that the operating temperature exceeds 90 °C.

3.2.7 Salts

If the salt concentration of the crude oil is over (1 lb/1000 bbls) of crude, consideration needs to be given to the problem of chloride fouling and corrosion caused by hydrochloric acid resulting from the hydrolysis of $MgCl_2$ and $CaCl_2$ in the distillation-tower crude preheating exchangers, as follows:

- In cases where the salt concentration is between 1 and 10 ptb, corrosion prevention measures should be provided.
- If the salt concentration is over 10 ptb, a desalter must be provided to reduce it to under 1 ptb, or it should be reduced to around 1 ptb and corrosion preventive measures provided.

3.2.8 Condensate

To prevent condensation of water and hence corrosion, the operating temperature at the top section of the atmospheric distillation tower is raised. Therefore, more economical materials can be used here.

3.2.9 High Temperature

Regarding material selection for high-temperature piping and reformer tubes used in the reforming furnace, selection should be made with consideration given to economy because of the very expensive materials used.

3.2.10 CO_2 Corrosion

Carbon steel has no corrosion resistance in wet reforming gas services at temperatures above 40 °C.

3.2.11 Amine Solution

The use of copper and copper alloys should be avoided. The corrosiveness of a rich amine solution is the highest in the case of hydrogen units and town gas units, where only CO_2 is handled, and moderate in the case of FCC units where $CO_2 + H_2S$ ($H_2S/(CO_2 + H_2S) = 0.01$) is handled, and lowest in the case of hydrodesulfurization, where only H_2S is handled. Equipment that undergoes maximum corrosion are lean/rich heat exchangers, regenerators, reboilers, reclaimers, and overhead condensers.

3.2.12 H_2S

Parts and components that come in contact with wet hydrogen sulfide should be provided with sulfide stress corrosion cracking prevention measures in accordance with the latest edition of NACE MR 01-75.

3.2.13 H_2SO_4

Sulfuric acid in concentrations above 85% by weight is usually not corrosive to carbon steel if temperatures are below 40 °C. Cold-worked metal (usually bends) should be stress relieved. Flow velocities above 1.2 m/s can destroy the protective iron sulfate film. Also, localized attack immediately downstream of piping welds has been attributed to a spherodized structure; a normalizing post-weld heat treatment at 870 °C is required to minimize corrosion.

All valves and pumps require corrosion-resistant internals or trim. In addition to sulfuric acid, reactor effluent contains traces of alkyl and dialkyl sulfates from secondary alkylation reactions. These esters decompose in reboilers to form sulfur dioxide and polymeric compounds, and finally sulfurous acids, which can cause severe corrosion in overhead condensers (particularly deisobutanizer towers). Neutralizers or filming amine corrosion inhibitors can be injected into the overhead vapor lines of various towers to prevent corrosion.

3.2.14 Hydrogen Fluoride

In general, hydrofluoric acid is less corrosive than hydrochloric acid because it passivates most metals. However, if these films are destroyed by dilution or something else, severe corrosion in the form of hydrogen blistering of carbon steel and stress cracking of hardened bolts will occur.

Specific areas where corrosion is likely to occur include the bottom of the acid rerun tower, the depropanizer tower, the overhead condensers of these towers, the reboiler of the propane stripper, and piping around the acid rerun tower.

By proper design practices to keep the feed stocks dry, and prescribed maintenance procedures to keep the equipment dry during shut-downs, there will be few corrosion problems with this catalyst.

3.2.15 Acetic Acid

Corrosion by acetic acid can be a problem in petrochemical process units. As a rule, even 0.1% water in acetic acid can have a significant influence on the corrosion rate.

Temperature increases the corrosion rate, bromide and chloride contamination causes pitting and SCC, while the addition of oxidizing agents, including air, can reduce the corrosion rate. Type 304 stainless steel can be use for temperatures below 90 °C and Type 316 and 317 for hot acetic acid applications.

3.2.16 Ammonia

Ammonia causes two types of SCC in petrochemical plants. The first is cracking of carbon steel in anhydrous ammonia service, and the second type is cracking of copper alloys. Use of low-strength steels, post-weld heat treatment of welds, and regular inspection are some actions that can be taken to minimize cracking. Cracking of copper alloy tube bundles during shut-downs should be prevented by neutralizing the residual ammonia with acid.

3.2.17 Fuel Ash

Corrosion by fuel ash deposits can be one of the most serious operating problems with boiler and preheat furnaces. All fuels except natural gas contain certain inorganic contaminants that leave the furnace with products of combustion. In particular, vanadium pentoxide vapor (V_2O_5) reacts with sodium sulfate (Na_2SO_4) to form sodium vanadate ($Na_2O.6V_2O_5$). This compound will react with steel, forming a molten slag that runs off and exposes fresh metal to attack.

In general, alloys with high chromium and nickel contents provide the best resistance to this type of attack. Also, the addition of magnesium-type compounds raises the melting points of fuel ash deposits and prevents the formation of highly corrosive films. These additives also offer additional benefits with regard to cold-end corrosion in boilers by condensation (150–170 °C) of sulfuric acid produced from the sulfur content of the fuel, by forming magnesium sulfate.

3.2.18 Micro-organisms

The corrosion action of sulfate-reducing bacteria (SRB) is well known in the oil industry, especially in cooling water systems, fire water loops, after hydrotesting of tanks and vessels, and in mothballed or water-flooded systems.

3.2.19 Special Material Requirements for Refinery Equipment

3.2.19.1 Austenitic Stainless Steel

The use of austenitic stainless steel should be kept to a minimum. When the use of such a material cannot be avoided and where there is danger of transgranular stress corrosion cracking, the use of higher alloy materials such as stabilized Incoloys or ferritic stainless steel such as Type 444 (18 Cr-2 Mo) should be considered.

3.2.19.2 Parts to be Welded

For parts to be welded, including tank plates and structural steel, no bottom or side air or enriched air-blown converter steels should be used. Oxygen-blown converter steel may be used only below the creep temperature range.

3.2.19.3 Copper-Based Alloy

The use of copper-based alloys in direct contact streams in which ammonia acetylene or its homologs may be present is prohibited.

3.2.19.4 Carbon Content

Carbon content and carbon equivalent, based on (C + Mn)/6 for any plain carbon or carbon manganese steel that is to be joined by welding, should not exceed 0.25% and 0.41%, respectively.

In cases where the above requirements are not met, welding procedure qualification tests in accordance with applicable codes should be performed, and welding procedures for the portions subjected to the tests should be submitted for agreement separately.

3.2.19.5 Ferritic Stainless Steel

The use of ferritic stainless steel should be considered on the basis of the following characteristics:

- Weldability
- Embrittlement at 474 °C (885°F)
- Pitting corrosion
- Caustic embrittlement.

3.2.20 Special Equipment Requirements for Pressure Vessels (Including Exchanger Shells, Channels, etc.)

3.2.20.1 Low-Temperature Vessels

When pressure vessels are subjected to low temperatures, i.e. below 0 °C, materials and fabrication practices, e.g. post-weld heat treatment, should be selected to minimize the risk of brittle fracture.

Requirements for material selection depend upon the minimum design temperature. However, where this minimum design temperature is not a normal continuous operating condition, for example, if it arises as a result of autorefrigeration due to rapid depressurization, the full range of temperatures and coincident pressures should be evaluated in order to determine the appropriate conditions for material selection.

The use of post-weld heat treatment can extend the use of carbon steel to temperatures lower than would be acceptable for as-welded vessels. However, unless post-weld heat treatment is required for process reasons, it should be specified only when the requirement cannot be met by using carbon steel in the as-welded condition.

3.2.20.2 Corrosion Resistance

Carbon steel should normally be selected for pressure vessels, and an appropriate corrosion allowance applied where total corrosion is not expected to exceed 6 mm over the design life of the vessel. Where the corrosion rate is predicted to exceed this, the various alternatives should be evaluated. These may include, but should not be limited to, the following:

- Replacement at intervals, e.g. every 12 years
- Increased corrosion allowance
- Corrosion-resistant internal linings
- Alternative solid corrosion-resistant material.

Where pressure vessels are relatively thin in the absence of any corrosion allowance, the use of solid corrosion-resistant alloys such as stainless steel and nickel-based alloys may be more suitable than corrosion allowances or the use of internal cladding. However, for thicker vessels it is likely that internal corrosion-resistant alloy cladding will provide the most economical solution. In certain circumstances, the use of coal tar epoxy, glass-flake reinforced resins or other non-metallic coatings may be appropriate. The followings should be considered where there is a choice between cladding or lining, and solid corrosion- resistant material:

- The alloy material of vessel shells and heads required for corrosion resistance may be provided as alloy-clad plate or as alloy plate, provided that the backing material of the clad plate is suitably resistant to the other conditions of the designated process.
- The choice between alloy plate or alloy-clad plate should be made based on economic considerations. However, when austenitic stainless steel is the material required for corrosion resistance, alloy cladding should be used.
- The use of alloy sheet lining, instead of cladding or deposit lining, for vessel shells and heads should be subject to separate approval and considered only for localized areas where the use of lining may be desirable from an economic standpoint.
- For heavy shells and heads, alloy deposit lining may be used in lieu of cladding. The automatic strip-arc deposit welding process is acceptable. In all overlay weld metal the ferrite content should be between 4 and 5%.
- Where the anticipated erosion-corrosion rates on carbon steel wear plates exceed 1.5 mm per year, alloy steel wear plates should be employed to prevent this corrosion rate being exceeded.
- Cast iron pressure-retaining parts should not be used in process fluid services, but may be used in fresh cooling water services for heat exchanger channels and cover sections.
- Strip-clad plate should not be used if post-weld heat treatment is required.

3.2.21 Storage Tanks

The decision on steel used for storage tanks should be made from an economic viewpoint, between either normal or high tensile steel; however, the yield strength of the plate, weld metal, and heat-affected zone should be 60 kg/mm^2 maximum. Steels containing deliberately added chromium, nickel, or molybdenum should not normally be used for tankage. Austenitic stainless steels should not be used for swing arm cables.

3.2.22 Heat Exchanger Tube Bundles

Materials for heat exchanger tubes and tube sheets should be selected for resistance against both shell and tube side fluids. Allowances for corrosion should be made on both sides of single tube sheets. For water-cooled heat exchangers, the following considerations should be made.

3.2.22.1 Seawater-Cooled Heat Exchanger

For heat exchangers on seawater duty, where long life is required, titanium may be used. Alternatively, Cu/Ni alloys may be selected, provided that the fluid velocities are kept within the range given in the specifications. Normally, seawater is permitted only on the tube side of a heat exchanger. On some high-pressure gas coolers, however, this is not possible because of the risk of tubes collapsing under external pressure. In such cases titanium tubes and shells are necessary to allow seawater to be used on the shell side.

Where the materials of interconnecting seawater piping and the mating surfaces of the heat exchanger are dissimilar, rubber-lined couplings will be required if galvanic corrosion would otherwise occur. This is particularly important in the case of titanium and Cu/Ni dissimilar metal joints. An alternative solution that may be considered is the use of sacrificial spool pieces of austenitic spheroidal graphitic cast iron between the titanium and Cu/Ni components.

Titanium plate exchangers should be used in closed-circuit systems where treated freshwater is exchanged with seawater.

Whether tubes will be either inhibited aluminium brass or aluminium bronze, the tube sheets should be of the same material as the tubes.

Where corrosion of copper-based alloys by sulfides in the hydrocarbon stream is excessive, consideration should be given to either providing a greater corrosion allowance than normal or to the use of materials such as nickel-based alloys (such as Monel, Incoloy 801), aluminum alloys (such as Alclad), and titanium alloys.

3.2.22.2 Freshwater-Cooled Heat Exchanger

Carbon steel tubes may be used only where the water has a low dissolved solid content and where a water recirculation system is employed. Copper-based alloys subject to stress corrosion cracking in hydrocarbon streams containing free ammonia (with pH exceeding 7.2, even for short periods) should not be employed in heat exchangers. Cu-Ni (70-30) alloy may be considered satisfactory for such applications.

For hydrocarbon/hydrocarbon heat exchangers, where one or both hydrocarbon streams have a high H_2S content, consideration should be given to the use of double-dip-aluminized material contact with liquids in order to prevent corrosion due to sulfide scale fouling.

Unstabilized austenitic stainless steel should not be used for U-tubes; low carbon unstabilized stainless steels such as Type 304L or Type 316L are acceptable. Normally, air-cooled heat exchanger tubes should be carbon steel. For corrosive or heavy fouling services, the application of internal coatings should be considered, if required.

3.2.23 Furnaces

Material for furnace tubes should be selected from an economic viewpoint. However, high- temperature strength, corrosion resistance, and scaling-resistance factors must be satisfied. Furnace tube wall thickness, material selection, and calculations should be based on 100 000 hours operation, in accordance with API RP 530.

Corrosion rates in excess of 0.5 mm per year are not normally acceptable. The design corrosion rate of furnace tubes should be determined on the basis of available information from corrosion experience in similar applications. In the absence of any suitable information, a minimum corrosion allowance of 3.2 mm should be provided for furnace tubing in hydrocarbon services, and 1.6 mm in steam services.

Material selected for furnace tubes and other parts of furnace coils exposed to firebox conditions should be such that free-scaling temperatures will not be exceeded under normal operation.

The composition, and physical and mechanical properties of materials for headers and return bends, irrespective of whether they are cast or wrought, rolled or welded in, should be compatible with those tubes to which they will be connected and be of a weldable quality. The use of cast alloy steel parts should require approval.

Carbon steel tubes for steam generating units should be seamless.

3.2.24 Piping

Materials for piping should be selected from an economic viewpoint; however, strength based on the pressure-temperature rating against corrosion resistance should be satisfied. Where high alloy or non-ferrous material is employed, special consideration should be given to decide the economical limits of the pipe size for which a clad or solid design is to be adopted.

3.2.25 Low-Temperature Piping

Where piping systems are subjected to low temperatures, i.e. below 0 °C, materials and fabrication practices, e.g. post-weld heat treatment, should be selected to minimize the risk of brittle fracture.

3.2.26 Corrosion-Resistant Piping

Where carbon steel is the selected material for piping, and the total corrosion is not expected to exceed 6 mm over the design life of the piping, an appropriate corrosion allowance should be applied. Where the corrosion rate is predicated to exceed 6 mm, alternatives should be evaluated. These alternatives may include, but should not be limited to, the following:

1. Replacement at intervals, e.g. every 10 years
2. Increased corrosion allowance
3. Application of internal corrosion-resistant cladding
4. Alternative solid corrosion-resistant material
5. Injection of a corrosion inhibitor, or other treatment of the process stream.

Where the choice is between options 3 or 4, selection will generally be governed by cost. However, austenitic stainless steel in solid form should be used in a marine environment only where the external skin temperature does not exceed 50 °C, and should normally be AISI Type 316, because of the risk of chloride stress corrosion cracking.

Where the external skin temperature exceeds 50 °C, carbon steel lines internally clad with austenitic stainless steel may be used. Alternatively, solid pipe of one of the duplex stainless steels may used, as they exhibit much greater resistance to chloride stress corrosion cracking. They also possess much higher yield strengths, and their use therefore results in weight saving.

Where carbon steel vessels or pipework are connected to pipework that is either internally clad or of solid corrosion-resistant alloy, and where galvanic corrosion of the carbon steel is likely, such corrosion should be prevented by installing electrically isolating joints, insulating flanges, or pipe spools coated internally with a non-metallic lining, whichever is appropriate for the conditions. It should be noted that, in many locations, insulating flanges and joints will be rendered ineffective by electrical short circuiting through connections to the supporting steelwork.

Piping for seawater duty should normally be of 90/10 Cu/Ni conforming to the piping specification. High molybdenum austenitic and 25% Cr duplex stainless steels may offer cost and weight advantages over Cu/Ni, and should be evaluated for specific projects.

These stainless steels have, in addition to much higher strength, excellent resistance to pitting corrosion, chloride stress corrosion cracking and flow-induced erosion and, therefore, may permit the use of higher flow velocities, which in turn may permit the use of smaller bore piping, and thinner pipe walls, thus saving weight and cost. Recent limited laboratory testing indicates that the stainless steels may be susceptible to chloride crevice corrosion in seawater at temperatures above about 30 °C. This should be taken into consideration for piping downstream of heat exchangers.

Non-metallic materials, such as glass reinforced plastics (GRP), may offer advantages for seawater pipework, particularly with respect to corrosion resistance and weight saving. However, specialist expertise in design, fabrication, and installation techniques will be required for the evaluation of factors such as cost, susceptibility to mechanical damage, and safety implications, before such materials are selected. Any proposal to use non-metallic materials should be subject to approval. Also, it may be necessary to obtain waivers from the statutory authorities regarding the use of combustible materials.

3.2.27 Corrosion-Resistant Valves

In general, valve bodies and bonnets should be manufactured in a material similar to that used for the piping or vessel to which they are attached. Valve trims should be manufactured in a more resistant material to prevent erosion/ corrosion; the choice of materials being dependent upon the process conditions.

Where electroless nickel plating of valve internals is approved by the company (e.g. for ball valves or parallel slide gate valves), the following requirements should be met:

- The substrate should be stainless alloy for high integrity valves, e.g. those for sub-sea applications, although carbon steel may be permitted for other applications.
- The phosphorous content of the coating should be within the range 8 to 11% by weight.
- Plating thickness should be not less than 0.075 mm. Components should not be baked after plating.
- Plated components should be subjected to a ferroxyl test to ASTM B 733 for evidence of porosity or cracking.
- Plated test pieces should be sectioned and checked for coating thickness using a micrometer.
- The adhesion of the nickel coating should be evaluated using coated test pieces subject to testing in accordance with ASTM B 733 and ASTM B 571.

3.2.28 Flare Systems

For high-pressure flares of the Indair type, alloy 800 H should be used for the bowl and stool. For Mardair type flares, Incoloy DS should be used for the trumpet. The gas-filled parts and base may be fabricated in alloy 800 H; however, AISI Type 316 may be used if there is a heat shield in incoloy DS with ceramic fiber insulation.

3.2.29 Rotating Machinery

Generally, pump casings are fabricated in a material matching that used for the piping system. Pump internals are usually fabricated in corrosion-resistant materials with additional resistance to erosion, the choice of materials being dependent upon the process conditions.

Pumps handling seawater or brine above 40 °C contaminated with oil and H_2S should be fabricated in one of the super duplex stainless steels or a more corrosion-resistant material. When a wet gas stream is corrosive, the first stage of wet gas compressors should be fabricated in a corrosion-resistant material such as 13% Cr steel.

Exhaust stacks for gas turbines should be fabricated in corrosion-resistant carbon steel. Also, stacks should be protected externally by an aluminum metal spray with an aluminum silicone sealer. Care should be taken to ensure that the design eliminates thermal fatigue.

3.2.30 Special Material Requirements in Petrochemical Plants

In selecting materials for petrochemical plants, considerable effort should be paid to fluid composition, sizing of lines, valve and pump details, and processing temperature and pressure. Most environments in petrochemical processes involve flammable hydrocarbon systems, highly toxic chemicals, explosive gases, and strong acids and caustics. Therefore corrosion could be a mysterious and costly enemy to the safety of personnel and community.

Table 3.1 shows materials used in different processes of a petrochemical plant. However, such tables are just informative, and material and corrosion allowances should be selected on the basis of the corrosion tests and procedures outlined in relevant standards.

3.2.31 Supplemental Requirements for Equipment in Sour Service

Equipment in sour service, as set forth in the process data sheet or in the mechanical drawings, should strictly comply with the requirements of NACE/6/ standard MR 0175, as supplemented by the following.

Table 3.1 *Index of piping services*

Service	Rating-face temperature & pressure	Basic material	Valve body/ trim	Corrosion allowance
Caustic (stress relieved)	Class 150.rf	Carbon steel	Carbon steel Monel	3.18 mm (0.125″)
General process	Class 150.rf 399 °C (750 °F) max.	Carbon steel	Carbon steel 11-13 Cr	None
Corrosive process	Class 150.rf 399 °C (750 °F) max.	304 SS	316 SS	None
Mildly corrosive process	Class 150.rf 399 °C (750 °F) max.	Carbon steel	Carbon steel 316 SS	2.54 mm (0.10″)
Corrosive process	Class 150.rf 99 °C (750 °F) max.	Carbon steel	Carbon steel 316 SS	3.13 mm (0.125″)
Corrosive process	Class 150.rf 399 °C (750 °F) max.	Carbon steel	Carbon steel 316 SS	6.0 mm (0.251″)
Low-temperature process	Class 150.rf −46°C to −30 °C (−50 °F to −21 °F)	LTCS	316 SS & LTCS	None
Urea solution/melt process vapor condensate	Class 150.rf 427 °C/800 °F max.	304 l SS	316 l SS	None
Urea solution/melt process vapor condensate	Class 150.rf 427 °C/800 °F max.	316 l SS	316 l SS	None
Steam & boiler feed water condensate	Class 150.rf 399 °C (750 °F) max.	Carbon steel	Carbon steeluniversal	1.27 mm (0.05″)
Lube and seal oil	Class 150.rf 66 °C (150 °F) max.	304 SS	Carbon steel	None
General process	Class 300.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel 11-13 Cr	None
Hydrogen & hydrocarbon	Class 300.rf 593 °C (1100 °F) max.	1 1/4 Cr-1/2 Mo	1 1/4 Cr- 1/2 Mo 11-13 Cr	1.27 mm (0.05″)
Corrosive process	Class 300.rf 399 °C (750 °F) max.	304 SS	316 l SS	None
Mildly corrosive process	Class 300.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel 316 SS	2.54 mm (0.10″)
Corrosive process	Class 300.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel 316 SS	3.18 mm (0.125″)
Low-temperature process	Class 300.rf −46 °C to −30 °C (−50 °F to −21 °F)	LTCS	316 SS & LTCS	None
Steam & boiler feed water condensate	Class 300.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel universal	1.27 mm (0.05″)
Lube and seal oil	Class 300.rf 66 °C (150 °F) max.	304 SS	Carbon steel	None
Urea solution/melt process	Class 300.rf 427 °C/800 °F max.	304 l SS	316 l SS	None
Urea solution/process vapor condensate	Class 300.rf 427 °C/800 °F max.	316 l SS	316 l SS	None
General process	Class 600.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel 11-13 Cr	None

(*continued overleaf*)

Table 3.1 *(continued)*

Service	Rating-face temperature & pressure	Basic material	Valve body/ trim	Corrosion allowance
Hydrogen & hydrocarbon	Class 600.rf 593 °C (1100 °F) max.	1 1/4 Cr-1/2 Mo	1 1/4 Cr- 1/2 Mo 11-13 Cr	1.27 mm (0.05″)
Corrosive process	Class 600.rf 399 °C (750 °F) max.	304 SS	316 SS	None
Corrosive process	Class 600.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel 316 SS	3.18 mm (0.125″)
Steam & boiler feed water condensate	Class 600.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel universal	1.27 mm (0.05″)
Steam & boiler feed water	Class 600.rf 593 °C (1100 °F) max.	1 1/4 Cr-1/2 Mo	1 1/4 Cr-1/2 Mo universal	1.27 mm (0.05″)
Lube & seal oil	Class 600.rf 66 °C (150 °F) max.	304 SS	Carbon steel 11-13 Cr	None
General process	Class 900.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel 11-13 Cr	None
Low-temperature process	Class 900.rf −46 °C to −30 °C (−50 °F to −21 °F)	LTCS	316 SS	None
Steam & boiler feed water	Class 900.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel Full HF	1.27 mm (0.05″)
Steam & boiler feed water	Class 900.rf 593 °C (1100 °F) max.	1 1/4 Cr-1/2 Mo	1 1/4 Cr-1/2 Mo Full HF	1.27 mm (0.05″)
Lube & seal oil	Class 900.rf 66 °C (150 °F) max.	304 SS	Carbon steel 11-13 Cr	None
Urea solution Carbonate solution CO_2, process vapor	Class 1500.lrj 399 °C (750 °F) max.	316 l SS	316 l SS Ferroalum	None
General process	Class 1500.rj 427 °C (800 °F) max.	Carbon steel	Carbon steel 11-13 Cr	None
Hydrogen & hydrocarbons	Class 1500.rj 593 °C (1100 °F) max.	1-1/4 Cr-1/2 Mo	1 1/4 Cr- 1/2 Mo Full HF	1.27 mm (0.05″)
Steam & boiler feed water	Class 1500.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel Full HF	1.27 mm (0.05″)
Steam & boiler feed water	Class 1500.rj 593 °C (1100 °F) max.	1-1/4 Cr-1/2 Mo	304 H SS	None
Steam & boiler feed water	Class 2500.rj 816 °C (1500 °F) max.	304 H SS	1 1/4 Cr/HF	1.27 mm
Steam-jacketed urea melt	Class 150.rf 427 °C (800 °F) max.	304l/CS JKT	Carbon steel 316 SS	None
Plant air	Class 150.ff 66 °C (150 °F) max.	Carbon Steel	CI/MI CI/13% Cr	1.27 mm (0.05″)
Vacuum exhaust	Class 125.ff 177 °C (350 °F) max.	Carbon steel	Carbon steel universal	1.27 mm (0.05″)

Table 3.1 *(continued)*

Service	Rating-face temperature & pressure	Basic material	Valve body/ trim	Corrosion allowance
Cooling water (above ground)	Class 125.ff 66 °C (150 °F) max.	Carbon steel	Carbon steel/ cast iron	1.27 mm (0.05″)
Cooling water (above ground)	Class 125.ff 66 °C (150 °F) max.	Carbon steel	Carbon steel/ cast iron	1.27 mm (0.05″)
Cooling water (underground)	Class 125.ff 66 °C (150 °F) max.	Carbon steel	CI/MI/CI	1.27 mm (0.05″)
Demineralized water	Class 150.ff 204 °C (400 °F) max.	304 SS	316 SS	None
Urea solution process vapor/condensate	Class 600.rfsf 427 °C (800 °F) max.	316 l SS	316 SS	None
Potable water (above ground)	Class 125.ff 66 °C (150 °F) max.	Galv. CS	CI/MI/CI	None
Potable water (underground)	150 psig max. 66 °C (150 °F) max.	PVC	PVC	None
Fire water (above ground)	Class 125.ff 66 °C (150 °F) max.	Carbonsteel	Carbon steel/CI	
Fire water (underground)	Class 125.ff 66 °C (150 °F) max.	Carbon steel	CI/NI/CI	
Instrument air supply	Class 150.ff 66 °C (150 °F) max.	Carbon steel	CI/NI/ 11-13 Cr	None
Steam tracing	5.30 kg/cm^2 (75 psig) max. 316 °C (600 °F) max.	316 SS	–	1.27 mm (0.05″)
Instrument process & analyzer service	233.08 kg/cm^2 (3600 psig) 399 °C (750 °F) max.	316 SS	316 SS	None
Instrument air signal	14.06 kg/cm^2 (125 psig) ambient temp.	CS/316 SS	CS/ 11-13 Cr	None
Instrument process piping	104 kg/cm^2 (1480 psig) ambient temp.	CS/304 SS	Carbon steel/ 11-13 Cr	1.27 mm (0.05″)
Instrument process piping	202 kg/cm^2 (2880 psig) ambient temp.	CS/304 SS	Carbon steel/ 11-13 Cr	1.27 mm (0.05″)
Sewer (non-corrosive)	Atmospheric ambient temp.	DI		None
Sewer (corrosive)	Atmospheric ambient temp.	Vitrif1-clay		None
Sewer (Benfield and urea solution)	Atmospheric 260 °C (500 °F) max.	304 l SS		None
Steam-jacketed urea melt	Class 300.rf 427 °C (800 °F) max.	CS/304 l SS	316 SS	None
H_2SO_4 (93–98%)	Class 150.lj −29 °C to 230 °C (−20 °F to 466 °F)	TFE-lined CS	DI/PFA-lined	None

(*continued overleaf*)

Table 3.1 *(continued)*

Service	Rating-face temperature & pressure	Basic material	Valve body/ trim	Corrosion allowance
Raw water (above ground)	Class 125.ff 66 °C (150 °F) max.	Carbon steel	Carbon steel/ cast iron	2.4 mm
Raw water (above ground)	Class 125.ff 66 °C (150 °F) max.	Carbon steel	Carbon steel/ cast iron	2.4 mm
Raw water (underground)	Class 125.ff 66 °C (150 °F)	Ductile iron	CI/MI/CI	None
Hydrochloric (28%)	Class 150.ff −29 °C to 66 °C (−20 °F to 150 °F)	Saran lined	DI/PFA-lined	None
Mildly corrosive process	Class 600.rf 427 °C (800 °F) max.	Carbon steel	Carbon steel/ 316 SS	2.4 mm (0.1″)
High-temperature sewer (non-corrosive)	Atmospheric	DI		None
Corrosive process alloy verified	Class 300.rf 399 °C (750 °F) max.	304 SS	316 SS	None
Hydrogen & hydrocarbon	Class 600.rf 593 °C (1100 °F) max.	1 1/4 Cr-1/2 Mo	1 1/4 Cr/ 13% Cr HF	1.27 mm (0.05″)

Note:
Saran = polyvinylidene chloride, saran fiber
MI = malleable iron
CI = grey cast iron
DI = ductile iron
TFE = poly tetrafluoroethylene
PFA = perfluoro alkoxy copolymer

3.2.32 Carbon Steel

3.2.32.1 Process of Manufacture

All carbon steel products should be fully killed and fine-grain treated and should be supplied in normalized, normalized and tempered, or quenched and tempered condition. Production should be by a low-sulfur and low-phosphorus refining process (e.g. electric furnace with double deslagging or in the basic oxygen converter). The heat should be vacuum degassed and inclusion shape control treated, preferably by calcium.

3.2.32.2 Chemical Analysis

Chemical analysis should be restricted as follows:

- *Check analysis*
  - Carbon 0.020 % max.
  - Sulfur 0.003 % max.
  - Phosphorus 0.020 % max.
  - Manganese 1.20 % max.
  - Silicon 0.45 % max.

- *Heat analysis*
  - Carbon 0.190 % max.
  - Sulfur 0.002 % max.
  - Phosphorus 0.020 % max.
  - Manganese 1.20 % max.
  - Silicon 0.45 % max.
- *Residuals*
  - Chromium 0.25 % max.
  - Copper 0.25 % max.
  - Molybdenum0.10 % max.
  - Nickel 0.30 % max.
  - Vanadium0.05 % max.
  - Niobium0.04 % max.
  - Ca + O + N to be reported
- *Carbon equivalent (CE)*
  CE should not exceed 0.42%.

$$\mathrm{CE}(\%) = \mathrm{C} + \frac{\mathrm{Mn}}{6} + \frac{(\mathrm{Cr} + \mathrm{Mo} + \mathrm{V})}{5} + \frac{(\mathrm{Ni} + \mathrm{Cu})}{15} \tag{3.19}$$

3.2.32.3 Through-Thickness Tension Testing

Plates 25 mm and greater in thickness, directly exposed to sour environments (see NACE MR 0175 par. 1.3) should have a minimum reduction of area of tension test specimens (Z value) of 35%. Testing should be conducted according to ASTM A-770.

3.2.32.4 Ultrasonic Testing

Ultrasonic testing, in accordance with ASTM A-435, should be carried out on all plates having a thickness greater than 12 mm.

3.2.32.5 Hardness

Hardness across the width and thickness of each product/weld should not exceed 200 HB. Specimens for hardness surveys should be taken in the same area as the coupons are to be removed for mechanical tests.

3.2.32.6 Weld Ability Tests

It should be demonstrated that the proposed plates are suitable for welding and subsequent post-weld heat treatment by carrying out weldability tests on representative plates. The hardness value in the heat affected zone should not exceed 200 HB. Details of these tests should be provided for company approval.

3.2.32.7 Stainless Steel

Stainless steel products should be supplied in fully solution-treated condition. Cold working resulting in a material deformation degree of more than 5% should be followed by a solution annealing heat treatment of the parts involved.

3.2.33 Fabrication Requirements

All carbon steel vessels should be post-weld heat treated after completion of all welding. Minimum temperature should be 595 °C as stated in NACE MR 0175. This condition will lead to specify a PWHT target temperature of 615 ± 20 °C.

Internal and external fittings, and attachments welded to pressure parts, should be fully penetrated. Nozzles should be self-reinforced with integral or welding-neck flanges.

Hardness testing should be conducted on the base metal, weld metal, and heat affected zone, as follows:

- Test macro-examination specimens taken from production test coupons.
- Test internal welds of the equipment (one set reading for each longitudinal and/or circumferential shell weld, at least).
- Hardness value should not exceed 200 HB.

Because of the significantly greater risk of crevice corrosion in sour/chloride service, the use of screwed couplings and some types of weld details, which could result in a crevice on the process side, is not permitted.

C – ½% Mo welding consumables and those having more than 1% Ni should not be used for welding carbon-manganese steel.

Weld repair of plate surface defects should not be permitted without approval, and should be subject to an agreed repair procedure prior to the work being carried out.

4

Engineering Materials

Today's engineers have a vast range of materials, comprising several thousand, available to them. Also, parallel to the invention of new and improved materials, there have been equally important developments in materials processing, including vacuum melting and casting, new molding techniques for polymers, ceramics, and composites, and new joining technology.

In addition to the need for an increased knowledge of materials and technology, other challenges are having to be met by material engineers. In earlier times, with a much smaller number available, engineers often selected materials for their designs by a process of trial and error, in many cases using more material than was really necessary. Today there is a requirement for knowledge about the materials to use them more effectively and efficiently in order to minimize cost.

4.1 The Range of Materials

The complete range of materials can be classified into four categories:

- Metals
- Polymers
- Ceramics and inorganic glasses
- Composites.

The classification "Composites" contains materials with constituents from any two of the first three categories.

4.2 Properties of Engineering Materials

A broad comparison of the properties of metals, ceramics, and polymers is given in Table 4.1. Very many properties, or qualities, of materials have to be considered when choosing a material to meet a design requirement (see Table 4.2).

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Table 4.1 *Comparison of the properties of metals, ceramics, and polymers*

Property	Metals	Ceramics	Polymers
Density (kg/m^3)	2000–16000 (ave. 8000)	2000–17000 (ave. 5000)	1000–2000
Melting points	Low to high e.g. Sn 232 °C, W 3400 °C	High, up to 4000 °C	Low
Hardness	Medium	High	Low
Machinability	Good	Poor	Good
Tensile strength (MPa)	Up to 2500	Up to 400	Up to 120
Compressive strength (MPa)	Up to 2500	Up to 5000	Up to 350
Young's Modulus (GPa)	40–400	150–450	0.001–3.5
High-temperature creep resistance	Poor	Excellent	–
Thermal expansion	Medium to high	Low to medium	–
Thermal conductivity	Medium	Medium, but often decreases rapidly with temperature	Very low
Thermal shock resistance	Good	Generally poor	–
Electrical properties	Conductors	Insulators	Insulators
Chemical resistance	Low to medium	Excellent	Generally good
Oxidation resistance at high temperatures	Poor, except for rare metals	Oxides excellent, SiC and Si_3N_4 good	–

Table 4.2 *Material properties and qualities*

Physical properties	Density, melting point, hardness; elastic modulus; damping capacity
Mechanical properties	Yield, tensile, compressive, and torsional strength; ductility; fatigue strength; creep strength; fracture toughness
Manufacturing properties	Ability to be shaped by moulding and casting, plastic deformation, powder processing, machining; ability to be joined by adhesives, welding, etc.
Chemical properties	Resistance to oxidation, corrosion, solvents, and environmental factors
Other non-mechanical properties	Electrical, magnetic, optical, and thermal
Economic properties	Raw material and processing costs; availability
Esthetic properties	Appearance, texture, and ability to accept special finishes

These include a wide range of physical, chemical, and mechanical properties, together with forming, or manufacturing characteristic, cost and availability data, and in addition, more subjective esthetic qualities such as appearance and texture. Some of these values for different materials are given in Table 4.3. Although it is not the purpose of this book to give detailed coverage of the properties of all materials, we will briefly discuss those materials used in moderately large quantities in oil industries.

Table 4.3 *Properties (at 25 °C) of some groups of materials*

Material	E (GPa)	Yield strength (MPa)	Tensile strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	Density ($kg/m^3 \times 10^{-3}$)
Steels	200–220	200–1800	350–2300	80–170	7.8–7.9
Cast irons	150–180	100–500	300–1000	6–20	7.2–7.6
Aluminum alloys	70	25–500	70–600	5–70	2.7–2.8
Copper alloys	90–130	70–1000	220–1400	30–120	8.4–8.9
Magnesium alloys	40–50	30–250	60–300	–	1.7–1.8
Nickel alloys	180–220	60–1200	200–1400	> 100	7.9–8.9
Titanium alloys	100–120	180–1400	350–1500	50–100	4.4–4.5
Zinc alloys	70–90	50–300	150–350	–	6.7–7.1
Polyethylene (LDPE)	0.12–0.25		1–16	1–2	0.91–0.94
Polyethylene (HDPE)	0.45–1.4		20–38	2–5	0.95–0.97
Polypropylene (PP)	0.5–1.9		20–40	3.5	0.9–0.91
PTFE	0.35–0.6		17–28	–	2.1–2.25
Polystyrene (PS)	2.8–3.5		35–85	2	1–1.1
Rigid PVC	2.4–4		24–60	2.4	1.4–1.5
Acrylic (PMMA)	2.7–3.5		50–80	1.6	1.2
Nylons (PA)	2–3.5		60–100	3–5	1.05–1.15
PF resins	5–8		35–55	–	1.25
Polyester resins	1.3–4.5		45–85	0.5	1.1–1.4
Epoxy resins	2.1–5.5		40–85	0.3–0.5	1.2–1.4
GFRP	10–45		100–300	20–60	1.55–2
CFRP	70–200		70–650	30–45	1.4–1.75
Soda glass	74		50*	0.7	2.5
Alumina	380		300–400*	3–5	3.9
Silicon carbide	410		200–500*	–	3.2
Silicon nitride	310		300–850*	4	3.2
Concrete	30–50		7*	0.2	2.4–2.5

*Modulus of rupture value.

4.3 Corrosion Prevention Measures

To select required materials for a given process, functionally and economically, feasible protective measures should also be considered.

Basically, protection comprises those measures providing separation of metal surfaces from corrosive environments, or those that allow adjustment or altering of the environment. The following sections give an outline of corrosion prevention measures.

4.3.1 Cathodic Protection

Cathodic protection (Figure 4.1) is possible only when the structure to be protected and the auxiliary anode are in both electronic and electrolytic contact.

A reduction in metal to electrolyte potential of −0.850 V (saturated copper sulfate electrode as reference) is specified as the necessary potential that must be obtained for either optimum or absolute protection of ferrous structures in soil or water. Cathodic protection is applied by one of two methods, power impressed current or sacrificial anodes.

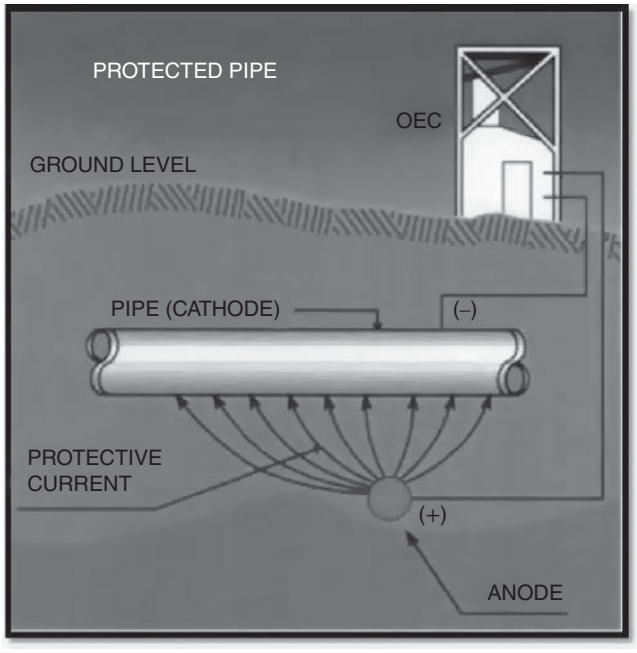


Figure 4.1 *Cathodic protection system.*

4.3.2 Coating, Painting, and Lining Materials

More metal surfaces are protected by coating, painting, and lining than by all other methods combined. Coatings, paintings, and linings that act as a protective film to isolate the substrate from the environment exist in a number of different forms. Therefore, the selection of a proper corrosion resistance system depends on a number of factors.

4.3.3 Inhibitors

Altering the environment provides a versatile means of reducing corrosion. Typical changes in medium thatare often employed in the petroleum industry are:

- lowering temperature
- decreasing velocity
- removing oxygen or oxidizer
- filtration
- changing concentration of corrosives
- use of corrosion inhibitors.

An inhibitor is a substance that, when added in small concentrations to an environment, decrease the corrosion rate considerably. To be fully effective all inhibitors are required to be present above a certain minimum concentration.

Corrosion inhibitors can be divided into different categories. Among these, the most used class in the oil industry is film-forming. The effect of a film-forming inhibitor is to establish a molecular layer just on the steel surface and then a second hydrophobic layer of aliphatic tails. Therefore water cannot

reach the steel surface and promote corrosion. The efficiency of an inhibitor in reducing corrosion depends on concentration, rate of dispersion, film persistency, velocity, temperature, pH, flow regime, presence of disturbances able to perturbate the flow, and fluid composition.

4.4 Material Selection Procedure

This section of analysis deals with the procedure and order of appreciation, evaluation, and selection of materials both for their functional suitability and for their ability to sustain this positive function for the required length of time at a reasonable cost. Considering the profusion of materials and material-oriented literature, this procedure is, of necessity, schematic (Figure 4.2).

It attempts only to indicate the system of parallel evaluation of corrosivity of different petroleum environments, the effect of process parameters, estimation of corrosion rates, determination of corrosion allowances for a given life, and a few guidelines in selection of materials in conjunction with corrosion control measures and economic principals.

Figure 4.3 shows schematic corrosion control used for material selection.

However, the knowledge of materials is so vast and far-reaching that close cooperation of the designer with metallurgists, material engineers, corrosion engineers, and other materials specialists is stressed.

4.5 Guidelines on Material Selection

Materials should be selected based on functional suitability and ability to maintain function safely at a reasonable cost for an economical period of time. The particular material selected should be be accurately determined.

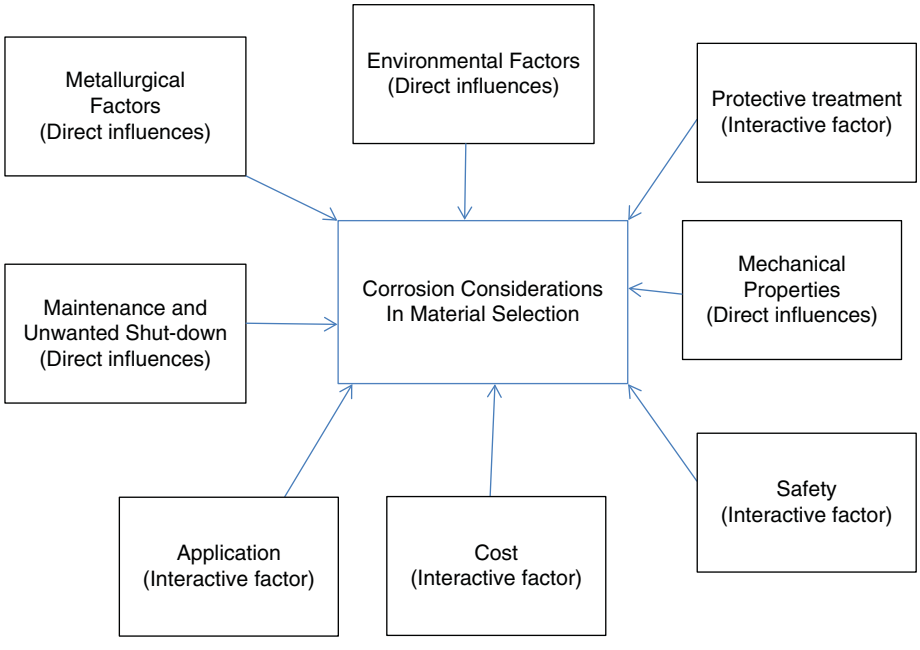


Figure 4.2 *Corrosion considerations in material selection.*

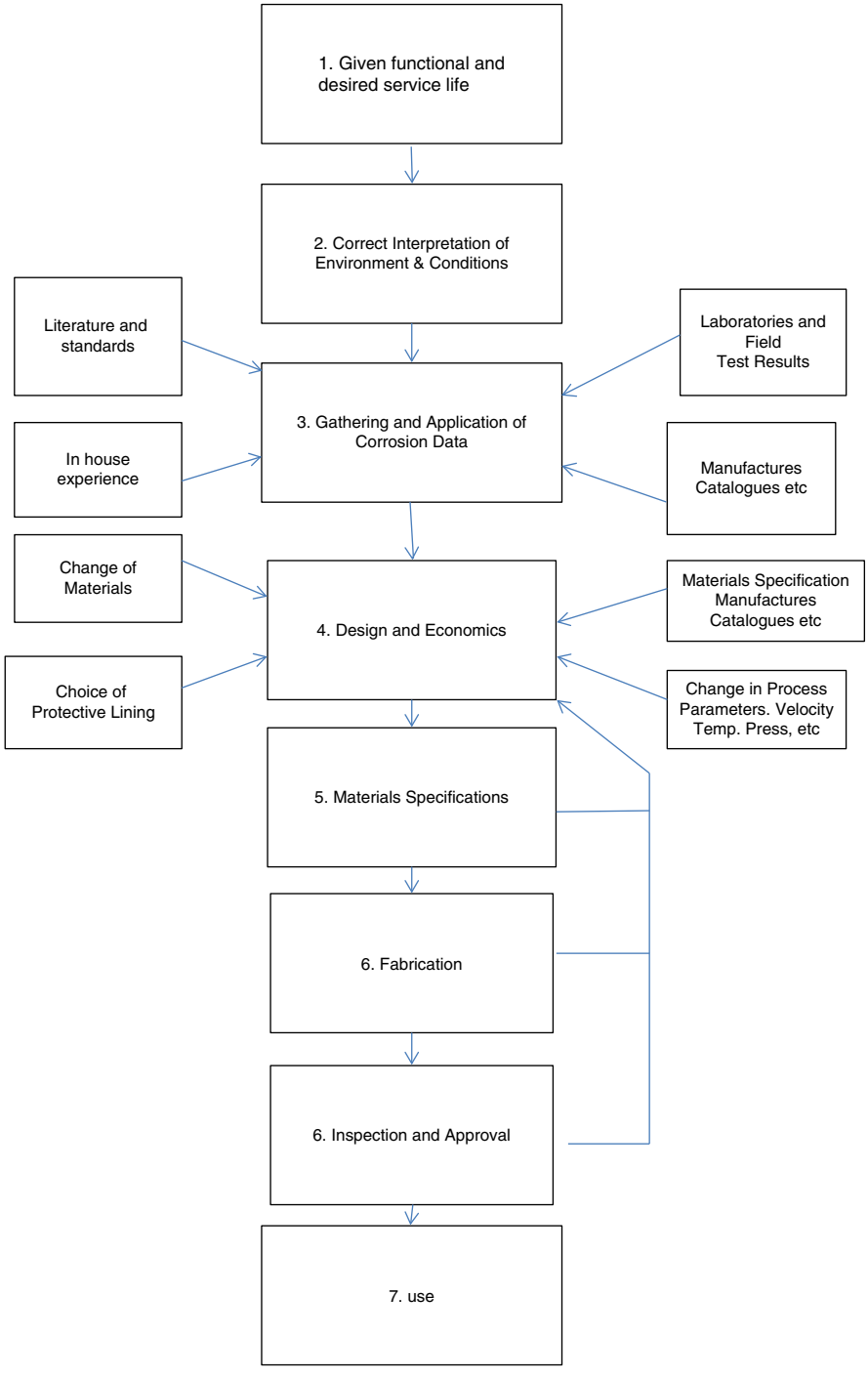


Figure 4.3 *Schematic of corrosion control used for material selection.*

The whole material complex should be considered, as an integrated entity, rather than each material separately. The more highly resistant materials should be chosen for the critical components and where relatively high fabrication costs are involved. It may be necessary to compromise and sacrifice some mechanically advantageous properties to satisfy corrosion requirements, and vice versa.

Where the corrosion rate is either very low or very high, the choice of materials is simple; where it is moderately low, a thorough analysis of all aspects is required.

In dry environments and carefully controlled fluids, many materials can be used – and these often may be left unprotected. Under atmospheric conditions, even polluted atmospheres, such metals as stainless steels and aluminum alloys do not need protection. Also, copper and lead have long lives. In a more severe wet environment, for example in marine conditions, it is generally more economical to use relatively cheap structural materials (mild steel) and apply additional protection, rather than use more expensive options. For the severest corrosive conditions it is preferable in most cases to use materials resistant to the corrosive, than to use cheaper material with expensive protection.

Materials more expensive than absolutely necessary should not be chosen unless it is economical in the long run and necessary for safety of personnel or product, or for other important reasons. Using fully corrosion-resistant materials is not always the correct choice, a balance between the initial cost and the cost of subsequent maintenance should be found over the full estimated life of the designed utility.

Certain combinations of metal and corrosive are a natural choice:

- Aluminum – non-staining atmospheric exposure
- Chromium-containing alloys – oxidizing solutions
- Copper and alloys – reducing and non-oxidizing environments
- Hastelloys (chlorimets) – hot hydrochloric acid
- Lead – dilute sulfuric acid
- Monel – hydrofluoric acid
- Nickel and alloys – caustic, reducing, and non-oxidizing environments
- Stainless steels – nitric acid
- Steel – concentrated sulfuric acid
- Tin – distilled water
- Titanium – hot, strong oxidizing solutions
- Tantalum – ultimate resistance.

The composition of an alloy alone does not ensure the quality of the product. Evaluation of resistance to corrosion in a given environment, adverse effects of corrosion products on utility or contents, susceptibility to a specific type of corrosion and fouling, and tendency to corrosion failure due to fabrication and assembly processes, such as welding, forming, machining, heat treatment, etc., are of prime importance for the selection of material.

Due consideration shouls be given to special treatments required to improve resistance to corrosion, e.g. special welding techniques, stress relieving, blast peening, metallizing, sealing of welds, etc., and also to any fabrication or assembly methods that would aggravate any tendency of the material to corrosion failure.

Alloys in as highly alloyed a condition as necessary should be used when the cost of fabrication is higher than the cost of the basic material. The proportional cost of material in some multi-shaped or complicated components is much less than in simple ones.

An alloy or temper should be selected that is free of susceptibility to localized corrosion under the respective general and local environmental conditions in the utility, and that meets the strength and fabrication properties required for the job. It is sometimes better to use a somewhat weaker, but less sensitive, alloy, than to use one that does not lend itself to reliable heat treatment and, due to this, whose resistance to a particular form of corrosion is poor.

If heat treatment after fabrication is not feasible, the materials and method of fabrication chosen should give optimum corrosion resistance in the as-fabricated condition. Materials prone to stress corrosion cracking should be avoided in environments conducive to failure, observing that stress relieving alone is not always a reliable cure.

When corrosion or erosion is expected, an increase in the wall thickness of the structure or piping should be provided over that required by other functional design requirements. This allowance, in the judgment of the designer, should be consistent with the expected life of the structure or piping. The allowance should ensure that various types of corrosion or erosion (including pitting) do not reduce the thickness below that required for the mechanical stability of the product. Where no thickening can be allowed or where lightening of the product is contemplated, a proportionally more corrosion-resistant alloy or better protection measure should be used.

Short-life materials should not be mixed with long-life materials in non-reparable subassemblies. Materials forming thick scale should not be used where heat transfer is important.

Where materials could be exposed to atomic radiation it is necessary to consider whether the effect will be derogatory or beneficial, observing that some controlled radiation may enhance the property of a metal.

Not only the structural materials themselves, but also their basic treatment should be evaluated for suitability (e.g. chromate passivation, cadmium plating, etc.) at the same time.

Non-metallic materials complying with the following requirements are preferred: low moisture absorption, resistance to fungi and microbes, stability through temperature range, compatibility with other materials, resistance to flame and arc, freedom from outgassing and ability to withstand weathering.

Flammable materials should not be used in critical places; the heat could affect the corrosion stability of structural materials. Materials producing dangerous volumes of toxic or corrosive gases when under fire or high-temperature conditions should not be used.

Fragile or brittle materials that are not, by design, protected against fracture should not be used in corrosion-prone spaces. Materials that produce corrosion products that can have an adverse effect on the quality of the contents should not be used, especially when the cost of the wasted contents exceeds the cost of the container.

All efforts should be made to obtain from the suppliers of equipment an accurate detailed description of the materials used within their products. The following should be noted with regard to electrical equipment:

- The use of hygroscopic materials and of desiccants should be avoided. The latter, when their use is necessary, should not be in contact with an unprotected metallic part.
- Fasteners should be of a well-selected corrosion-resistant material, or materials better protected than the parts they join together.
- Materials selected should be suitable for the purpose and be either inherently resistant to deterioration or adequately protected against deterioration by compatible coatings, especially in problem areas where corrosion can cause low conductivity, noise, short circuits, or broken leads, thus leading to degradation of performance.
- Insulation materials used should not be susceptible to moisture. Stainless steels or precipitation hardening stainless steel should be passivated.

4.6 Procedure for Material Selection

The first step in material selection is a thorough review of the corrosive environment, process parameters, and equipment operating conditions, including temperature, pressure, flow rates, liquid versus gaseous phase, aqueous verses anhydrous phase, continuous verses intermittent operation, media used for cooling or heating, etc.

In the second step, the corrosion rate (CR) should be predicted and the corrosion allowances (CA) determined for the service life of the equipment and its various components in carbon steel.

For the third step, if the determined total wall thickness (mechanical + CA) is not acceptable, great effort should be exercised to select and evaluate a suitable corrosion prevention measure to lower the required corrosion allowance. Some of these measures cannot withstand the process conditions, e.g. temperatures too high for polymer lining, no facilities for chemical injection, no continuous electrolyte for cathodic protection, and so on.

In the fourth step, if the preventive measures cannot reduce the corrosion rates of carbon steel to an acceptable level, then a more corrosion-resistant material should be considered. Many materials can be immediately excluded because of service conditions.

The fifth step, if required, is to conduct standard test methods to evaluate the nominated materials in a simulated environment. These tests give assurance to the right selection.

The sixth step involves the evaluation of the cost of materials for the service life of the plant and also a comparison between the costs of using an expensive material and using a cheaper one plus a protective measure.

When the construction materials have been selected, the preparation of a clear and concise specification to ensure that the material is fabricated and obtained as ordered, and meets the requirement of the specific material standards is mandatory. Any problem associated with fabrication of equipment with the selected material or rejection during inspection should be reported to allow re-analysis and ratification of the selection and specification.

It should be realized that specified material may fail owing to undesirable or unknown properties induced during fabrication or installation, such as metallurgical changes, inclusion and chemical composition changes, etc. Measures that may be required to prevent or limit such factors (e.g. special heat treatment) are outside the scope of this book.

4.7 Process Parameters

The major factors controlling corrosion in the oil and gas industries are:

- The CO_2 partial pressure
- The H_2S partial pressure
- The fluid temperature
- The water cut
- The water salinity
- The flow dynamics
- The pH of the solution.

It must be emphasized that corrosion is likely to occur only in the water phase. Vaporized water in streams at temperatures above the dew point are considered non-corrosive.

4.8 Corrosion Rate and Corrosion Allowances

The corrosion rate is the uniform decrease in thickness of a material per year. The corrosion allowance, expressed in terms of thickness, is a measure of extra thickness with which a material can survive its design life. Therefore, to determine a suitable material with enough corrosion allowance for the design life of a plant, firstly the corrosion rate should be predicted. This is possible by:

- calculation
- corrosion abstracts and data survey handbooks
- experience and in-house data

- material vendors' data
- equipment fabricators
- testing of materials.

4.8.1 Calculation

Many different formula, nomograms, curves, and software, based on laboratory or field experience, exist to evaluate the general corrosion rate. Results obtained following these approaches should be considered the "worst case corrosion rate" or R_{max}.

This rate may be adjusted by considering the influence of the rest of the environment. The final corrosion rate may be thus expressed as:

$$R_{corr} = R_{max} \times F_s \times F_i \times F_c \times F_o \times F_w \times F_{pH} \tag{4.1}$$

where:

F_s = scale factor
F_i = inhibition factor
F_c = condensation factor
F_w = percentage of water factor
F_o = percentage of oil factor
F_{pH} = pH factor

4.8.2 Corrosion Study by Literature Survey

In corrosion studies undertaken for the purpose of finding a suitable material to withstand a particular service, it is best to first take advantage of the vast amount of published literature in the field of corrosion. Such a study will in general give a very good clue as to the general types of metals or alloys that should prove most satisfactory for a particular job.

NACE; The Corrosion Data Survey Handbook, has two sections: metals and non-metals. There are more than 50000 points of data (Nelson method) on the performance of metallic and non-metallic construction materials in corrosive environments.

4.8.3 Corrosion Tests

Corrosion tests are the best appropriate technique for acquisition of data for material selection. In most corrosion data survey handbooks, corrosion rates are evaluated for just a few factors (e.g. temperature and concentration). However, there are many other factors that influence corrosion rates. While they are often extremely important, it is impossible to list them all in a review of this type.

4.8.3.1 Test Methods

Corrosion tests are primarily aimed at the acquisition of data in a relatively short time compared to service lifetime, to predict service behavior. Corrosion test methods may be divided into three categories:

- Laboratory tests
- Pilot-plant tests
- Full-size equipment tests.

Service situations are complicated by many factors, such as velocity, temperature, pressure, aeration, heat flux, the presence of oxidizing agents, partial pressure of corrosive gases, inhibitor

concentration etc., which can either increase or decrease the corrosion rate. This may cause pilot-plant exposure tests to be preferable to laboratory tests.

4.8.3.2 The Need for Testing

The necessity for corrosion testing depends on:

- the degree of uncertainty after available information has been considered
- the consequences of making a less-than-optimum selection
- the time available for evaluation.

Therefore a company material/corrosion engineer should determine when and which type of tests are required.

4.8.3.3 Pilot-Plant Tests

These tests give more information for a preliminary selection of materials than most laboratory tests. Test conditions are more like the final application, and therefore the results are more reliable.

4.8.3.4 Full-Size Tests

Reliability is further enhanced when it is possible to test full-size components fabricated from the candidate material.

4.8.3.5 Laboratory Tests

In some cases laboratory testing is the only means for final material selection. The initial laboratory tests on the selected materials should be as simple as possible. Depending on the nature of the environment in which the material is to be used, at least the more important corrosion controlling factors should be simulated in tests.

Briefly, a test on metallic material should at least cover the following:

- Actual fluids should be used or mixtures simulating them
- Test coupons should be provided from the selected material
- Generally, experimental time is approximately one week
- Microscopic examination is essential to look for local attack.

For non-metals, the test should cover:

- Weight, volume, hardness, strength, and appearance changes, before and after exposure
- Generally, the test period is 1–3 months.

In any laboratory test great care shall be taken in the interpretation of the data. At best the results can only be qualitative and a great deal of common sense and experience has to be applied to such results before they become useful to the engineer.

Although it is not the intention here to catalog the various standard test methods in detail, those listed below may be helpful where and when required.

4.8.3.6 Standard Corrosion Test Methods

Such test methods can be used to compare the many variables in material composition, manufacturing, and field performance. The tests also can be used to compare different types of material, or the same material grade from various manufacturers using different manufacturing process, and to evaluate different corrosion control measures. However, the objective set of variables for the test dictates the selection of test methods. Therefore, a careful study of both process and material (physical,

chemical, and mechanical) properties and the type of protective measure (e.g. inhibition) is usually required to make the proper selection of a test method.

4.8.3.7 Reporting Test Results

Test results should be tabulated to indicate at least the following:

- Chemical composition of material
- Heat treatment
- Pre-test metallurgy
- Post-test metallurgy
- Estimated corrosion rate
- Type of localized attack (if any)
- pH of test solution
- Other information pertinent to the evaluation of the material, such as pressure, temperature, additives to the test solution, etc.
- Method of corrosion rate calculation.

4.9 Corrosion Allowance

$$\text{CA (mm)} \geq \text{Life (year)} \times \text{CR (mm/yr)} \tag{4.2}$$

where:
CA = corrosion allowance
CR = corrosion rate.

The minimum corrosion allowance to be considered for a piece of equipment depends on the required service life multiplied by the expected corrosion rate under process conditions.

According to Equation (4.2), the classes shown in Table 4.4 should be considered for equipment with a design life of 20 years.

Where the corrosion rate is more than 0.3 mm/yr, or the total corrosion over the design life exceeds 6 mm, other alternatives should be evaluated. These alternatives may include the following:

- Replacement at intervals (e.g. every 10 years where the corrosion rate is 0.6 mm/y)
- Corrosion-resistant linings
- Alternative solid corrosion-resistant materials.

4.10 Selection of Corrosion-Resistance Alloys

Alloy selection, from a corrosion standpoint, can be considered to be a three-step process. First, resistance to general corrosion must be ensured, which is primarily a function of the chromium content

Table 4.4 *Corrosion allowances versus corrosion rate for 20 years service life*

Class	Average corrosion rate (mm/yr)	Corrosion allowance (mm)
A: mild corrosion	< 0.05	1
B: medium corrosion	0.05–0.15	3
C: severe corrosion	0.15–0.3	6

Table 4.5 *Guidelines for H_2S limits for generic corrosion-resistance alloys (CRA) classes*

Material	Max. chloride conc.(%)	Min. pH allowed *in situ*	Max. temp. (°C)	Max. H_2S partial press. (barg)
Martensitic stainless steels				
13Cr*	5	3.5	90	0.10
Austenitic stainless steels				
316	1	3.5	120	0.1
	5	3.5	120	0.01
	5	5	120	0.1
6Mo	5	3.5	150	1
	5	5	150	2
Duplex stainless steels				
22Cr	3	3.5	150	0.02
	1	3.5	150	0.1
25Cr	5	3.5	150	0.1
	5	4.5	150	0.4
Nickel alloys				
625		3.5		5
C276				≫5
Titanium		3.5		≫5

Notes:
The limits given assume complete oxygen free environments.
If one of the listed parameters exceeds the given limit, the need for testing of the material according to ISO 15156-3 should be evaluated.
The temperature limit may be increased based upon evaluation of specific field data and previous experience. Testing may be required.
*For SM13Cr testing has indicated that lower limits are required.

of the alloy. Second, resistance to localized attack also must be ensured, mainly a function of molybdenum content. Finally, resistance to environmental stress cracking is sought at the highest feasible strength level. Nickel content plays a principal role in this instance, particularly in providing resistance to anodic cracking.

The close correlation between pitting resistance and resistance to anodic cracking should be noted. This apparently results from the ease of crack initiation under the low-pH–high-chloride conditions found in pits. Therefore, higher molybdenum can also increase resistance to anodic cracking.

With the procedures given below, regions of alloy applicability can be shown as a qualitative function of environmental severity. This has been attempted in Table 4.5, in which an aqueous, CO_2-containing environment (hence low pH) has been assumed and the effects of temperature, chloride, and H_2S concentration are illustrated. The effect of yield strength is not shown, but if environmental cracking is the limiting factor, reducing the yield strength should extend applicability to more severe environments.

The reader should be cautioned that such a table is really more of a guide to alloy qualification than to direct selection for a particular application. Therefore, it may aid in developing a more efficient approach to alloy testing.

Where the corrosion problem is not general (uniform), and is localized, such as stress corrosion cracking, pitting, crevice, sulfide stress cracking, etc., the material selection should be on the basis of the specific corrosion problem. In these cases the selection procedure is to follow all parts of the above section, except for the corrosion rate calculation and corrosion allowance.

4.11 Economics in Material Selection

Corrosion is basically an economic problem. Thus, the corrosion behavior of materials is an important consideration in the economic evaluation of any project. The two extremes for selecting materials on an economic basis without consideration of other factors are:

- *Minimum cost*: Selection of the least expensive material, followed by scheduled periodic replacement or correction of problems as they arise.
- *Minimum corrosion*: Selection of the most corrosion-resistant material regardless of installed cost or life of equipment.

4.11.1 Cost-Effective Selection

This generally falls somewhere between these extremes and includes consideration of many other factors. In most instances, there will be different alternative materials that may be considered for a specific application. Calculation of true long-term costs requires estimation of the following:

- Total installation cost
- Service life
- Maintenance cost
- Time and cost requirement to replace or repair at the end of service life
- Cost of downtime to replace or repair
- Cost of inhibitors, extra facilities, or training required to assure achievement of predicted service life
- Time value of money
- Factors which impact taxation, such as depreciation and tax rates
- Inflation rate.

It should be realized that the costs of processed products, such as sheet, plate, sections, and forgings will be much higher than ingot. Every process and every heat treatment will give added value and increase the final material cost. Also the process of alloying will mean that, generally, the costs of alloys will be higher than those of unalloyed metals (see Tables 4.6 and 4.7)

4.11.2 Economic Evaluation Techniques

Several different techniques exist for economic appraisal of different materials and alternative corrosion control measures. Among these are the concepts of:

- internal rate of return (IROR)
- discounted pay back (DPB)
- present worth (PW), also referred to as net present value (NPV)
- present worth of future revenue requirements (PWRR)
- benefit–cost ratios (BCR).

Some of these techniques lack adequate sophistication; others are unduly complex and do not lend themselves readily to comprehension and use, especially in calculations. Generally, the applied method should embody accepted economic terminology at the accounting and managerial levels, so that a material/corrosion engineer's judgment can be properly expressed to and understood by project management.

Therefore, for economic evaluation, reference is made to the NACE Standard Method "RP-02-72, Direct Calculation of Economic Appraisal of Corrosion Control Measures," in which the excellent presentation of the subject matter makes it superfluous to enlarge on the factors to be considered in economic evaluation.

Table 4.6 *Estimated costs of some materials by mass and by volume*

Material	Cost($/kg)	Material	Cost ($/100 cm^3)
Germanium	365.75	Germanium	213.50
Silver	163.98	Silver	172.20
Cobalt	31.54	Cobalt	27.42
PTFE	12.25	Nickel	7.95
Nickel	8.93	Chromium	5.90
Chromium	8.31	Tin	4.43
Tin	6.06	Brass (sheet)	4.17
Titanium	5.41	Beryllium-copper	3.45
Brass (sheet)	5.02	Cadmium	2.94
Al/Cu alloy sheet	4.38	Phosphor bronze (ingot)	2.85
Beryllium-copper	3.90	18/8 stainless (sheet)	2.71
Nylon 66 (PA 66)	3.85	PTFE	2.63
18/8 stainless (sheet)	3.50	Copper (tubing)	2.45
Cadmium	3.40	Titanium	2.43
Phosphor bronze (ingot)	3.24	Copper (grade A ingot)	2.12
Magnesium (ingot)	2.89	Manganese	1.87
Acrylic (PMMA)	2.80	Brass (ingot)	1.84
Copper (tubing)	2.75	Al/Cu alloy sheet	1.30
ABS	2.63	Zinc (ingot)	0.81
Manganese	2.52	Lead (ingot)	0.67
Copper (grade A ingot)	2.38	Magnesium (ingot)	0.51
Brass (ingot)	2.18	Mild steel (sheet)	0.47
Amino resin thermoset	1.49	Nylon 66 (PA 66)	0.44
Aluminum (ingot)	1.37	Aluminum (ingot)	0.37
P-F thermoset	1.31	Acrylic (PMMA)	0.33
Silicon	1.24	Silicon	0.30
Polystyrene	1.12	ABS	0.28
Zinc (ingot)	1.12	Mild steel (ingot)	0.25
Polyethylene (HDPE)	1.09	Amino resin thermoset	0.23
Polypropylene (PP)	1.00	Cast iron	0.19
Natural rubber	0.98	P-F thermoset	0.16
Polyethylene (LDPE)	0.74	Polystyrene	0.12
Rigid PVC	0.72	Natural rubber	0.12
Mild steel (sheet)	0.60	Polyethylene (HDPE)	0.11
Lead (ingot)	0.60	Rigid PVC	0.11
Mild steel (ingot)	0.32	Polypropylene (PP)	0.09
Cast iron	0.26	Polyethylene (LDPE)	0.07
Portland cement	0.09	Portland cement	0.03
Common brick	0.07	Common brick	0.01
Concrete (ready mixed)	0.04	Concrete (ready mixed)	0.01

The costs are based on bulk quantities quoted in July 1991.
It is usual to see the cost of materials quoted per unit mass. This may give a misleading picture as often it is the volume of material that is important than its mass.

4.12 Materials Appreciation and Optimization

To indicate, approximately, the general trend of parallel appreciation of materials, selective check-offs are discussed in this section. These can, of course, vary for different materials or designs and a selective adjustment will be required.

It is obvious from the contents of these selection lists that a thorough expert knowledge is required, both in engineering and in corrosion control, to complete and evaluate the required data. Only very

Table 4.7 *Cost build-up (steel products)**

Material	Cost ($ per tonne)
Iron from blast furnace	210
Mild steel (ingot)	315
Mild steel (black bar)	490
Mild steel (cold drawn bright bar)	665
Mild steel (hot rolled sections)	498.75
Mild steel (hot rolled strip coil)	476
Mild steel (cold rolled strip coil)	593.25
Mild steel (galvanized sheet)	689.50
Austenitic stainless steel (cold rolled sheet)	3500
Iron from blast furnace	210

*These cost figures applied in July 1991.

seldom, and then mostly in simple or repetitive projects, can this task be left to an individual; normally, close cooperation of designer and corrosion or material engineer is needed, and both will have to bring into play their overall and specialized expertise.

The data obtained from such a selection list, after appropriate evaluation and comparative appreciation, should serve as a base for a decision as to whether the appreciated conglomerate of material and its fabrication methods are suitable for the considered purpose. Although in some cases a clear-cut confirmation of suitability may be secured, in many more cases several materials and methods may be evaluated before the optimal one is found. Even then, such materials will not always satisfy all required properties and under such circumstances the most satisfactory compromise should be accepted.

4.13 Corrosion in Oil and Gas Products

Corrosion occurrence has been widely experienced in the oil and gas industry. In the following, the main corrosion processes in oil and gas phases are discussed. First of all it must be emphasized that corrosion is likely to occur only in the water phase, as the oil phase is considered non-corrosive. Consequently, the presence of free water is necessary for corrosion to occur, i.e. vaporized water in streams at temperatures above the dew point are considered non-corrosive. In addition, it is necessary, especially for mixed-phase streams (oil + gas + water) to verify the water wetting of materials; if water is confined in the middle of the stream, or trapped by oil, no corrosion attack may develop.

The principle factors controlling corrosion are:

- the CO_2 partial pressure
- the H_2S partial pressure
- the fluid temperature
- the water salinity
- the water cut
- the fluodynamics
- the pH.

Additional factors influencing corrosion rates in petroleum refineries and petrochemical plants, including offsite facilities and pollution-control facilities are:

- Organic acids (naphthenic acids)
- Hydrogen (atomic)

- Amine solution
- Sulfur
- Sodium hydroxide
- Ammonia
- Hydrofluoric acid
- Glycol
- Cyanide
- Sulfuric acid
- Galvanic couple
- Stress (plus chlorides, caustic, ammonia, amines, polythionic acids)
- Bacteria
- Concentration of corrosives
- Aeration
- Heat flux
- Welding defects
- High-temperature oxidation and corrosion.

Some of these specific factors are discussed in cavitation/erosion:

- Erosion
- Fatigue
- Fouling
- Galvanic (metal-filled plastics)
- Impingement
- Stress cracking and crazing
- Thermal conductivity (W/(m.°C))
- Toxicity
- Transmittance (%)
- Unit weight (m^3/kg)
- Water absorption (24 h/l cm thick/%)
- Wearing quality:
  - inherent
  - given by treatment.

4.14 Engineering Materials

4.14.1 Ferrous Alloys

Some 94% of the total world consumption of metallic materials is in the form of steels and cast irons. This is also true in the oil industries, with a figure around 98%. Therefore the primary choice in any material selection is steel or cast iron, unless they cannot provide the design requirements.

4.14.2 Carbon Steels

The strength and hardness of steels vary considerably with both carbon content and type of heat treatment. Certain names, which relate to the carbon content, are used in connection with steels:

- *Mild or low-carbon steels* contain up to 0.3% carbon.
- *Medium-carbon steels* contain between 0.3 and 0.6% carbon. These may be hardened and tempered.

- *High-carbon steels or tool steels* contain 0.6% carbon and are always used in the hardened and tempered condition.

Table 4.8 gives some typical uses of carbon steels.

4.14.3 Surface Hardening

Generally, the toughness of a material decreases as the hardness increases. There are very many service conditions where the requirement is for a tough material of very high surface hardness, such as shafts and gears. Table 4.9 shows different methods to accomplish surface hardening.

4.14.4 Alloy Steels

The main effects conferred by specific alloying elements are given in Table 4.10. Major categories of steels are as follows:

4.14.4.1 Low-Alloy Steel

Contains up to 3 or 4% of one or more alloying elements and is characterized by possessing similar microstructures, and requiring similar heat treatment to, plain carbon steels, but improved strength and toughness over plain carbon steels with the same carbon content.

4.14.4.2 High-Strength Low-Alloy Steel

This is a group of low-alloy steels with a very fine grain size and tensile yield strengths between 350 and 360 MPa. This is achieved by addition of small, controlled amounts of Nb, Ti or Va.

4.14.4.3 High-Alloy Steels

High-alloy steels are those that possess structures and require heat-treatment that differ considerably from those of plain carbon steels. Generally they contain more than 5% of the alloying element. A few examples of some high alloy steels are:

Table 4.8 *Compositions and typical applications of steels*

Carbon %	Name	Applications
0.05	Dead mild steel	Sheet & strip for presswork, car bodies, tin-plate, wire, rod, tubing
0.08–0.15	Mild steel	Sheet & strip for presswork, wire and rod for nails, screws, concrete reinforcement bar
0.15		Case carburizing quality
0.1–0.3		Steel plate and sections, for structural work
0.25–0.4	Medium-carbon steel	Bright drawn bar
0.3–0.45		Shafts and high-tensile tubing
0.4–0.5		Shafts, gears, railway tyres
0.55–0.65	High-carbon steel	Forging dies, railway rails, springs
0.65–0.75		Hammers, saws, cylinder linings
0.75–0.85		Cold chisels, forging die blocks
0.85–0.95		Punches, shear blades, high-tensile wire
0.95–1.1		Knives, axes, picks, screwing dies and taps, milling cutters
1.1–1.4		Ball bearings, drills, wood-cutting and metal-cutting tools, razors

Table 4.9 *Surface hardening methods*

	Effect	Suitability	Method	Result	Applications
Carburizing	A high-carbon surface is produced on a low-carbon steel and is hardened by quenching	Suitable for plain carbon or alloy steels containing about 0.15% Carbon	Low-carbon steel is heated at 850–930 °C in contact with gaseous, liquid, or solid carbon-containing substances for several hours. The high-carbon steel surface produced is then hardened by quenching	Case depth is about 1.25 mm. Hardness after heat treatment is HRC 65 (HD 870). Negligible dimension change is caused by carburizing. Distortion may occur during heat treatment	Typical uses are for gears, camshafts and bearings
Nitriding	A very hard nitride-containing surface is produced on the surface of a strong, tough steel	Nitralloy steels containing aluminum; a typical nitriding steel contains 0.3% C, 1.6% Cr, 0.2% Mo, 1.1% Al. This steel is hardened by oil quenching from 900 °C and tempered at 600–700 °C before being nitrided	The steel is heated at 500–540 °C in an atmosphere of ammonia gas for 50–100 hours. No further heat treatment is necessary	Case depth is about 0.38 mm. Extreme hardness (HD 1100). Growth of 0.025–0.05 mm occurs during nitriding. Case is not softened by heating for long periods up to 420 °C. Case has improved corrosion	Typical uses are for valve guides and seatings, and for gears
Cyaniding	A carbon and nitride-containing surface is produced on a low-carbon steel and is hardened by quenching	Suitable for plain carbon or alloy steels containing about 0.15% Carbon	Low-carbon steel is heated at 870 °C in a molten 30% sodium cyanide bath for about one hour. Quenching in oil or water from this bath hardens the surface of the steel	Case depth is about 0.25 mm. Hardness is about HRC 65. Negligible dimension change is caused by cyaniding. Distortion may occur during heat treatment.	Typical uses are for small gears, chain links, nuts, bolts and screws

(*continued overleaf*)

Table 4.9 *(continued)*

	Effect	Suitability	Method	Result	Applications
Carbonitriding	Carbon and nitrogen are added to the surface of a low-carbon steel and permit hardening by an oil quench	Suitable for plain carbon steels containing about 0.15% Carbon	Low carbon steel is heated at 700–870 °C for several hours in a gaseous ammonia and hydrocarbon atmosphere. Nitrogen in the surface layer increases hardenability and permits hardening by an oil quench	Case depth is about 0.5 mm. Hardness after heat treatment is HRC 65 (HD 870). Negligible dimension change occurs. Distortion is less than in carburizing or cyaniding	Typical uses are for gears, nuts and bolts
Flame hardening	The surface of a hardenable steel or iron is heated by a gas torch and quenched	Steel containing 0.4–0.5% carbon or cast iron containing 0.4–0.8% combined carbon may be hardened by this method	A gas flame quickly heats the surface layer of the steel and a water spray or other type of quench hardens the surface	The hardened layer is about 3 mm thick. Hardness is HRC 50–60 (HD 500–700). Distortion can often be minimized	Used for gear teeth, sliding ways, bearing surfaces, axles and shafts
Induction hardening	The surface of a hardenable steel or iron is heated by a high-frequency electromagnetic field and quenched	Steel containing 0.4–0.5% carbon or cast iron containing 0.4–0.8% combined carbon may be hardened by this method	The section of steel to be hardened is placed inside an induction coil. A heavy induced current heats the steel surface in a few seconds. A water spray or other type of quench hardens the surface	The hardened layer is about 3 mm thick. Hardness is HRC 50–60 (HD 500–700). Distortion can often be minimized. Surface remains clean	Used for gear teeth, sliding ways, bearing surfaces, axles and shafts

Siliconizing (ihrigizing)	A moderately hard corrosion-resistant surface containing 14% silicon is produced on low-carbon steels	Suitable for plain carbon steels containing 0.1–0.2% carbon	The steel parts are heated at 930–1000 °C in contact with silicon carbide and chlorine gas for two hours. No further heat treatment is required	Case depth is about 0.63 mm. Hardness is about HD 200. Case has good corrosion resistance. Growth of 0.025–0.05 mm occurs during siliconizing	Typical uses are for valves, tubing and shafts
Hard chromium plating	A hard chromium plate is applied directly to the metal surface	Generally used on steels, low- or high-carbon, soft or hardened	The steel parts are plated in the usual plating bath, but without the undercoat of nickel. The plating is a thousand times thicker than decorative chromium plating	Plating thickness is about 0.125 mm. Extreme hardness HD 900. Plating has good corrosion resistance and a low coefficient of friction	Typical uses are for dies, gauges, tools and cylinder bores

Table 4.10 *Effects of alloying elements in steels*

Alloying element	General effects	Typical steels
Manganese	Increases the strength and hardness and forms a carbide; increases hardenability; lowers the critical temperature range, and when in sufficient quantity, produces austenitic steel; always present in a steel to some extent because it is used as a deoxidizer	Pearlitic steels (up to 2% Mn) with high hardenability used for shafts, gears, and connecting rods; 13% Mn in Hadfields steel, a tough austenitic steel
Silicon	Strengthens ferrite, raises the critical temperatures; has a strong graphitizing tendency; always present to some extent because it is used, with manganese, as a deoxidizer	Silicon steel (0.07% C; 4% Si) used for transformer cores; used with chromium (3.5%Si; 8% Cr) for its high-temperature oxidation resistance in internal combustion engine valves
Chromium	Increases strength and hardness, forms hard and stable carbides; raises the critical temperatures; increases hardenability; amounts in excess of 12% render steel stainless	1.0–1.5% Cr in medium- and high-carbon steels for gears, axles, shafts, and springs, ball bearings and metal-working rolls; 12–30% Cr in martensitic and ferritic stainless steels; also used in conjunction with nickel
Nickel	Marked strengthening effect, lowers the critical temperature range; increases hardenability; improves resistance to fatigue; strong graphite-forming tendency; stabilizes austenite when in sufficient quantity	0.3–0.4% C with up to 5% Ni used for crankshafts and axles, and other parts subject to fatigue
Nickel and chromium	Frequently used together in the ratio Ni/Cr = 3/1 in pearlitic steels; the good effects of each element are additive, each element counteracts the disadvantages of the other; also used together for austenitic stainless steels	0.15% C with Ni and Cr used for case carburizing; 0.3% C with Ni and Cr used for gears, shafts, axles and connecting rods; 18%, or more, of chromium and 8%, or more, of nickel give austenitic stainless steels
Tungsten	Forms hard and stable carbides; raises the critical temperature range, and tempering temperatures; hardened tungsten steels resist tempering up to 600 °C	Major constituent in high-speed tool steels; also used in some permanent magnet steels
Molybdenum	Strong carbide-forming element, and also improves high-temperature creep resistance; reduces temper-brittleness in Ni-Cr steels	Not normally used alone; a constituent of high-speed tool steels, creep-resistant steels and up to 0.5%Mo often added to pearlitic Ni-Cr steels to reduce temper-brittleness
Vanadium	Strong carbide-forming element; has a scavenging action and produces clean, inclusion-free steels	Not used on its own, but is added to high-speed steels, and to some pearlitic chromium steels

Table 4.10 *(continued)*

Alloying element	General effects	Typical steels
Titanium	Strong carbide-forming element	Not used on its own, but added as a carbide stabilizer to some austenitic stainless steels
Aluminum	Soluble in ferrite, also forms nitrides	Added to nitriding steels to restrict nitride formation on surface layers
Cobalt	Strengthens, but decreases hardenability	Used in Stellite-type alloys, magent steels, and as a binder in cemented carbides
Niobium	Strong carbide former, increases creep resistance	Added for improved creep resistance and as a stabilizer in some austenitic stainless steels
Copper	Increases strength and corrosion resistance. > 0.7% Cu permits precipitation hardening	Added to cast steels to improve fluidity, castability and strength. Used in corrosion-resistant architectural seels
Lead	Isoluble in iron	Added to low-carbon steels to give free-machining properties

- High-speed tool steels. High-carbon steels rich in tungsten and chromium provide wearing metal-cutting tools, which retain their high hardness at temperatures up to 600 °C. Example is 18/4/1 steel containing 18% tungsten, 4% chromium, 1% vanadium, and 0.8% carbon.
- Stainless steels. When chromium is present in amounts in excess of 12%, the steel becomes highly resistance to corrosion. There are several types of stainless steel which are summarized below.
- *Ferritic stainless steels*. Ferritic stainless steels contain between 12 and 25% chromium and less than 0.1% carbon. This type of steel cannot be heat treated, but may be strengthened by work hardening.
- *Martensitic stainless steels*. Steels of this class of steels contain between 12 and 18% chromium, together with a carbon content ranging from 0.1 to 1.5%. These steels can be *h*ardened by quenching from the austenite range of temperatures.
- *Austenitic stainless steels*. These are non-magnetic and contain 18% chromium, 8% nickel and less than 0.15% carbon. Carbides may form in these steels if they are allowed to cool slowly from high temperature, or if they are reheated in the range 500–700 °C (heat-affected zones adjacent to welds). Small stabilizing additions of titanium or niobium prevent the intercrystalline corrosion, weld decay. They are widely used in chemical engineering plant.
- *Maraging steels*. These are very high strength materials and can be hardened to give tensile strengths of up to 1900 MPa. They contain 18% nickel, 7% cobalt and small amounts of other elements, such as titanium. The carbon content is less than 0.05%. A major advantage of Maraging steels is that before the hardening process they are soft enough to be worked and machined, and precipitation-hardening treatment is at a fairly low temperature where distortion of machined parts is negligible. Although the basic material cost is very high, the final cost of a complex component is less than other high strength materials because of the much lower machining costs.
- *Manganese steels*. These are high-alloy steels that contain 12–14% manganese and 1% carbon. They are non-magnetic and are very resistance to abrasion, coupled with the fact that the core of material remains comparatively soft and tough. They are used for drill bits, rock crusher jaws, excavator bucket teeth etc.

4.15 Cast Iron

The carbon content of cast irons is generally between 2 and 4%. They are generally cheap, easy to melt and cast, with high damping capacity and very good machinability. Cast irons are classified as either white or gray. These terms arise from the appearance of a freshly fractured surface. The structure of cast irons is affected by the following factors:

- Rate of solidification
- Ccarbon content
- Presence of other elements
- Effect of heat treatment.

Table 4.11 indicates the composition and properties of some cast irons.

4.15.1 Malleable Irons

These cast irons are produced by heat treatment of certain white cast irons. There are two process used that give rise to black heart and white heart irons. The names arise from the appearance of the fracture surface of the treated iron. The white heart structure is composed of ferrite at the surface of casting, and ferrite, pearlite, and some graphite nodules at the center.

4.15.2 Alloy Cast Irons

Alloy cast irons are high strength, hard, and abrasion- and corrosion-resistant materials, and are suitable for high-temperature services. Addition of about 5% nickel causes the formation of martensitic

Table 4.11 *Composition and properties of some cast irons*

Approximate composition	Tensile strength (MN/m^2)	Type and uses
3.2% C, 1.9 % Si	250	Pearlite and graphite; motor brake drums
3.25 % C, 2.25 % Si	220	Pearlite and graphite; engine cylinder blocks
3.25 % C, 2.25 % Si, 0.35 % P	185	Ferrite, pearlite, and graphite; light machine castings
3.25 % C, 1.75 % Si, 0.35 % P	200	Ferrite, pearlite, and graphite; medium machine castings
3.25 % C, 1.25 % Si, 0.35 % P	250	Pearlite and graphite; heavy machine castings
3.6 % C, 2.8 % Si, 0.5 % P	370	Wear resistant; piston rings
3.6 % C, 1.7 % Si	540	Pearlitic; shaft and gear
3.6 % C, 2.2 Si	415	Ferritic; shaft and gear
2.8 % C, 0.9 % Si	310	Black heart malleable
3.3 % C, 0.6 % Si	340	White heart malleable
2.9 % C, 2.1 % Si, 1.75 % Ni, 0.8 % Mo	450	Shock resistant; crankshafts for petrol and diesel engines
2.9 % C, 2.1 % Si, 15 % Ni	220	Ni-resist; corrosion-resistant austenitic iron
2% Cr, 6% Cu	–	Used in chemical plant
2.5 % C, 5% Si	170	Silal; a growth-resistant iron for high-temperature service

structure at the surface of casting, which is very hard. The best cast iron for corrosion resistance has 15–25% nickel plus some chromium and copper. For prolonged service at elevated temperatures the carbon content of the alloy is kept down to about 2%, with 5% silicon, or silicon and nickel, the presence of which reduces oxide scale formation at high temperature.

4.16 Non-Ferrous Metals

All the other metallic elements (some 70 in number) and their alloys are classified as non-ferrous. Out of all the non-ferrous metals, only a few, aluminum, copper, lead, magnesium, nickel, tin, titanium, and zinc are produced in moderately large quantities. A brief description of non-ferrous metals and their alloys is given in following paragraphs; detailed coverage of the metallurgy of these metals is outside the scope of this book.

4.16.1 Aluminum

Aluminum possesses a number of properties that make it an extremely useful engineering material. It has good corrosion resistance, low density, and good electrical conductivity. The corrosion resistance of aluminum is due to the presence of a thin oxide layer that is only a few atoms in thickness, but it is permeable to oxygen and protects the surface from further attack.

The corrosion resistance may be improved by anodizing. High purity aluminum is too weak to be used for many purposes. The material commonly termed pure aluminum is an aluminum alloy, with up to 0.5% iron.

This small addition of iron gives a considerable increase in strength, although there is some reduction in ductility and corrosion resistance. Commercial-purity aluminum is used extensively, and accounts for a high percentage of aluminum product sales.

4.16.1.1 Aluminum Alloys

Aluminum may be alloyed with a number of elements to produce a series of useful engineering materials. For properties of some aluminum alloys and their uses see Table 4.12.

4.16.2 Copper

Copper is one of the oldest metals known to man and one of its alloys, bronze, has been worked for over 5000 years. Some applications of the various grades of pure copper are: wire, for electrical windings and wiring; sheet for architectural cladding, tanks and vessels and tubing for heat exchangers in chemical industries. There are very many useful applications of copper alloys in industries, but due to the price they have been replaced by cheaper material.

4.16.2.1 Copper Alloys

Copper may be alloyed with a number of elements to provide a range of useful materials. The important alloy systems are:

- copper–zinc (brasses)
- copper–tin (zinc) (bronzes and gun metals)
- copper–aluminum (aluminum bronzes)
- copper–nickel (capronickels).

Table 4.12 *Properties of some aluminum alloys*

Alloy number		Approximate composition	Condition	Tensile strength	Type of product	Uses
British	American					
1080	1060	99.99% Al 99.8% Al	Annealed	45 75	Sheet, strip	Linings for vessels in food and chemical plants
1200	1200	99% Al	Annealed	90	Sheet, strip, wire, extruded sections	Lightly stressed and decorative panelling, wire and bus bars, foil for packaging, kitchen and other hollow-ware
			Partly work hardened; Fully work hardened;	120 150		
3103	3103	Al + 1.75% Mn	Annealed	110	Sheet, strip, extruded sections	Hollow-ware, roofing, panelling, scaffolding tubing
			Partly work hardened; Fully work hardened;	160 210		
5251	5052	Al + 2% Mg	Annealed	180	Sheet, plate, tubes and extrusions	Stronger deep-drawn articles; ship and small boat construction and other marine applications
			Hardened and partially annealed	250		
5154A	5454	Al + 3.5% Mg	Annealed Hardened and partially annealed	240 300		
5056A	5056A	Al + 5% Mg	Annealed Hardened and partially annealed	280 335		
LM6	S12C	Al + 12% Si	As cast	180 Sand cast 210 Chill or die cast	Sand and die castings	Excellent casting alloy

6082	6082	Al + 0.9% Mg	Solution treated and naturally aged	220	Sheet, forgings, extrusions	Structural components for road and rail transport vehicles
		1% Si 0.7% Mn	Solution treated precipitation hardened	320		
2014	2014	Al + 4.5% Cu	Solution treated and naturally aged	440	Sheet, forgings, extrusions, tubing	Highly stressed parts in aircraft construction and general engineering
		0.5% Mg 0.8 % Mn	Solution treated precipitation hardened	480		
2024	2024	A1 + 4.5% Cu 1.5% Mg 0.6% Mn	Solution treated, cold worked and aged	480		
2L95		A1 + 5.6% Zn 1.6% Cu 2.5% Mg	Solution treated precipitation hardened	500	Plate, rod and bar, sheet and extrusions	Aircraft construction
L160						
7075	7075	A1 + 7% Zn 1.75% Cu 2% Mg	Solution treated precipitation hardened	620		
2090	2090	A1 + 2.2% Li 2.7 Cu 0.12% Zr	Solution treated precipitation hardened	580		
8090	8090	A1 + 2.5% Li 1.3% Cu 0.7% Mg	Solution treated precipitation hardened	495	Sheet plate	Aircraft construction

The addition of a small amount of berylium or chromium to copper produces high-strength alloys, a small addition of cadmium gives a significant increase in strength with little loss of electrical conductivity, while the addition of tellurium to copper yields an alloy with very good machineability. Properties of copper and some copper alloys are listed in Table 4.13.

4.16.3 Lead and its Alloys

Lead is soft and malleable, and possesses an excellent resistance to corrosion. It has been used for water pipework and waste disposal systems, but nowadays is replaced by other materials. A major application for lead is in the manufacture of lead–acid storage batteries which account for almost 30% of the annual world consumption of lead. Cable sheathing, soft solders, and fusible plugs in the sprinklers of fire-fighting systems are other applications of lead alloys (see Table 4.14).

4.16.4 Nickel

Pure nickel possesses an excellent resistance to corrosion by alkalis and many acids, and consequently, is used in chemical engineering plant. For cheapness, nickel is frequently used as a cladding of thin sheet on a mild steel base. Nickel may also be electroplated on a number of materials, and an intermediate layer of electrodeposited nickel is essential in the production of chromium-plated mild steel.

4.16.4.1 Nickel Alloys

The principal nickel-based alloys used industrially are Monel, Inconel, Incoloy, and the Nimonic series of alloys. Table 4.15 gives the composition and uses of some nickel alloys.

4.16.5 Titanium

The useful properties of titanium are its relatively high strength, coupled with a low density, and its excellent corrosion resistance. However it does possess some characteristics that make processing both difficult and costly. The main uses of titanium alloys are where excellent corrosion resistance is required.

4.17 Polymers

The group of materials known as polymers (or plastics) can be subdivided into thermoplastics, elastomers, and thermosetting materials. The use of plastic materials is increasing by a rate of 7% per annum. The major increase in the use of plastics is due to low cost, low densities, high resistance to chemical attack, good thermal and electrical insulation properties, and ease of fabrication. The main disadvantages are the low strength and elastic modulus values, low softening and thermal degradation temperatures,and their comparatively high thermal expansion coefficients. This section gives a brief general definition of the subdivisions of plastics.

4.17.1 Thermoplastics

There are several varieties of thermoplastics, but generally they have the property of softening with heating and hardening with cooling, within a temperature range (ASTM D 883). Thermoplastics are categorized as following (see also Table 4.16):

Table 4.13 *Properties of copper and some copper alloys*

Alloy	Approx. composition	Condition	Tensile strength (MPa)	Type of product	Uses
Pure copper	99.95% Cu	Annealed	220	Sheet, strip, wire	High conductivity electrical applications
		Work hardened	350		
Arsenical copper	99.85% Cu	Annealed	220	All wrought forms	Chemical plant, deep drawn and spun articles
		Work hardened	360		
Brasses	99.25% Cu 0.5% As	Annealed	220	All wrought forms	Retains strength at elevated temperatures
		Work hardened	360		
Gilding metal	90% Cu 10% Zn	Annealed	280	Sheet, strip	Heat exchange steam pipes
		Work hardened	510	Wire	
Cartridge brass	70% Cu 30% Zn	Annealed	325	Sheet, strip	Imitation jewellery and decorative work
		Work hardened	700		
General cold-working brass	65% Cu 35% Zn	Annealed	340	Sheet, strip, extrusions	High-ductility brass for deep drawing decorative work
		Work hardened	700		
Muntz metal	60% Cu 40% Zn	As manufactured (cast or hot worked)	375	Hot rolled plate and extrusions	General purpose cold working alloy
Bronzes	95.5% Cu 3% Sn 1.5% Zn	Annealed	325	Strip	Ships screws, rudders and high-tensile applications
		Work hardened	725		
	5.5% Sn 0.1% P balance Cu	Annealed	360	Sheet, strip, wire	British copper coinage
		Work hardened	700		
	10% Sn 0.5% P balance Cu	As manufactured (cast or hot worked)	280	Castings	Springs and steam turbine blades
Gunmetal	10% Sn 2% Zn balance Cu	As manufactured (cast or hot worked)	300	Castings	General purpose castings and bearings

(*continued overleaf*)

Table 4.13 *(continued)*

Alloy	Approx. composition	Condition	Tensile strength (MPa)	Type of product	Uses
Aluminum bronze	95% Cu 5% A1	Annealed	400	Strip, tubing	Pressure-tight castings, pump and valve bodies
		Work hardened	770		
	10% A1 2.5% Fe 2–5% Ni balance Cu	As manufactured (cast or hot worked)	700	Hot worked and cast products	Imitation jewellery and condenser tubes
Cupronickel	75% Cu 25% Ni	Annealed	360	Strip	High-strength castings and forgings
		Work hardened	600		
	70% Cu 30% Ni	Annealed	375	Sheet, tubing	British silver coinage
		Work hardened	650		
Monel	29% Cu 68% Ni 1.25% Fe 1.25% Mn	Annealed	550	All forms	Condenser tubing, excellent corrosion resistance
		Work hardened	725		
Beryllium–copper	1.75–2.5% Be 0.5% Co balance Cu	Solution heat treated and precipitation hardened	1300	Sheet, strip	Excellent corrosion resistance, used in chemical plants
Cadmium–copper	99% Cu 1% Cd	Annealed	285	Wire, rod	Springs, non-spark tools
		Work hardened	500		
Chromium–copper	0.4–0.8% Cr balance Cu	Solution heat treated and precipitation hardened	450	Wrought forms and castings	Overhead electrical wire, spot-welding electrodes, welding electrodes, commutal segments
Tellurium–Copper	0.3–0.7% Te balance Cu	Annealed	225	Wrought forms	Free-machining properties
		Work hardened	300		

Table 4.14 *Some lead alloys*

Alloy	Composition (%)					Applications
	Pb	Sb	Sn	Bi	Hg	
Antimonial lead	99	1	–	–	–	Cable sheathing
Hard lead	94	6	–	–	–	Lead–acid batteries, lead shot
Plumbers solder	60	2.5	37.5	–	–	
Common solder	50	–	50	–	–	Soft solders
Tinmans solder	38	–	62	–	–	
Type metal	62	24	14	–	–	For casting into printing type
Linotype metal	81	14	5	–	–	
Woods alloy	24	–	14	50	–	(+ 12% Cd) alloy with m.p. of 71° C used for fusible plugs in sprinkler systems
Roses alloy	28	–	22	50	–	Alloy with m.p. of 100 °C
Dental alloy	17.5	–	19	53	10.5	Dental cavity filling (m.p. 60 °C)

Table 4.15 *Composition and uses of some nickel alloys*

Alloy	Composition (%)										Uses
	Ni	Cu	Cr	Fe	Mo	W	Ti	Al	Co	C	
Monel	68	30	–	2	–	–	–	–	–	–	Chemical engineering plant, steam turbine blades
Inconel	80	–	14	6	–	–	–	–	–	–	Chemical engineering plant, electric cooker heating elements, exhaust manifolds
Brightray	80	–	20	–	–	–	–	–	–	–	Heating elements for kettles, toasters, electric furnaces
Hastelloy C	55	–	15	5	17	5	–	–	–	–	Chemical engineering plant
Hastelloy X	47	–	22	18	9	1	–	–	–	–	Furnace and jet engine components
Nimonic 75	77	–	20	2.5	–	–	0.4	–	–	0.1	Thermocouple sheaths, furnace components, nitriding boxes
Nimonic 90	56.6	–	20	1.5	–	–	2.4	1.4	18	0.06	Gas turbine discs and blades
Nimonic 115	56.5	–	15	0.5	4	–	4	5	15	0.1	Gas turbine discs and blades
Incoloy 825	45	3	22	25	3	–	1.2	0.2	–	0.05	Chemical engineering plant

- Polyethylene (PE): high-density (HDPE), low density (LDPE), linear low density (LLDPE), ultra high molecular weight (UHMWPE), cross linked (XLPE), and polyethylene foam
- Ethylene copolymers: ethylene–vinyl acetate (EVA), ionomers
- Polypropylene (PP)
- Polyvinyl chloride (PVC): unplasticized (UPVC), plasticized (PPVC), copolymers (CPVC and PVDC)
- Polytetrafluoroethylene (PTFE): ECTFE
- Polystyrene (PS): SBR, SAN, ABS
- Acrylic materials: PMMA, PAN
- Polyamides (nylon) (PA): PA 6, PA 6.6, PA 6.10, PA 6.12, PA 11, PA (R1M)
- Poly carbonate (PC)
- Acetal polyoxymethylene (POM)
- Saturated polyesters: PET, PETP, PCDT, PBT
- Cellulosics : (CN), CA, CAB, CP, EC
- Polyether ether ketone (PEEK)
- Polyphenylenes: PPO, PPS
- Polysulfones and polyarylates: PSU, PES, PPSU, PPS
- Polyimides (PI): PEI, PAI.

4.17.2 Elastomers

Elastomers are materials that have a low elastic modulus and show great extensibility and flexibility when stressed, but return to their original dimensions, or almost so, when the deforming stress is removed. There are several classes of elastomers, these being (see also Table 4.16):

- Natural rubber (NR)
- Synthetic R class elastomers (unsaturated carbon chains)
- M class elastomers (saturated)
- O class elastomers (heterochain with oxygen)
- U class elastomers (heterochain with O, N)
- Q class elastomers (heterochain with Si)
- Thermoplastic elastomers.

4.17.3 Thermosetting Materials

Thermosetting materials undergo chemical changes when first heated and are converted from a plastic mass into a hard and rigid material. There are also a number of materials that will set hard and rigid at ambient temperatures. The commercially available thermosetting materials are as follows:

- Phenolic materials, phenol formaldehyde
- Amino-formaldehyde materials, urea (UF), melamine (MF)
- Polyester materials
- Epoxies
- Polyurethanes
- Allyl resins, diallyl phthalate (DAP).

4.18 Ceramics and Glasses

Table 4.16 gives a summary of some of the main groupings of ceramic and glass materials.

Table 4.16 *Classification of some non-metallic materials and their maximum working temperature*

Class	Chemical classification	Some trade names	Abbrev. (ASTM/BS/ DIN/ISO)	Max. working temp. (°C)
Thermoplastic materials	Polyethylene, low density	Carlona, Lupolen, Alkathene	PE	60
	Polyethylene, high density	Carlona, Moplen, Alkathene	PE	70
	Polypropylene	Carlona P, Moplen, Propathene	PP	110
	Polychloride, plasticized	Mipolam	PVC	60
	Polyvinyl chloride, rigid	Carina, Vinidur, Geon	PVC	70
	Polychloro-trifluoroethylene	Kel-F, Hostaflon C	PCTFE	200
	Polytetrafluoroethylene	Teflon TFE, Hostaflon, Fluon	PTFE	260
	Polyvinyl alcohol	Elvanol, Mowiol	PVAL	90
	Polymethyl methacrylate	Perspex, Plexiglas	PMMA	70
	Polyacrylonitrile	Orlon, PAN	PAN	230
	Polyoxymethylene/ polyformaldehyde	Deirin, Celcon	POM	120
	Polychloromethyloxetane	Pentun	–	120
	Polystyrene	Carinex, Polystyrol	PS	70
	Polyamide	Aktrion, Nylon, Risan	PA	120
	Polyisobutylene	Rhepanol, Oppanol	PIB	100
	Chlorosulfonated polyethylene	Hypalon	CSM	180
	Fluorinated ethylene	Teflon FEP	FEP	200
	Acrylonitrile butadiene styrene	Cycolac, Kralastic	ABS	80
	Poly vinylidene chloride	Saran	PVDC	70
	Cellulose acetate butyrate	Cellidor B, Tenite butyrate	CAB	70
	Polyvinylidene fluoride	Solef, Kynar	PVDF	140
Thermosetting materials	Polyester, saturated	Terylene, Dacron	–	130
	Polyester, unsaturated, general purpose	Platal, Lamellon	UP	90
	Polyester, unsaturated, specific purpose	Atlac, Crystic	–	130
	Polyester, unsaturated, chlorinated	Hetron, HET	–	120
	Phenolics	Kera, Bomum harz 5102/6101, Keebush M/G	–	140
	Phenolics, modified	Haveg 31, Bomum harz 5104, Kera A	–	140
	Phenol formaldehydes	Haveg 41	PF	140
	Phenol furfurals	Haveg 60, Keebush H	–	140
	Furanes	Haveg 61, Bomum harz 6201, Kera FU	–	140
	Ureas	Plastopal, Plaskon	UF	125

(*continued overleaf*)

Table 4.16 *(continued)*

Class	Chemical classification	Some trade names	Abbrev. (ASTM/BS/ DIN/ISO)	Max. working temp. (°C)
	Melamines	Formica, Ultrapas	MF	130
	Silicones	Baysilon	SI	250
	Polyurethanes	Durethan U	PUR	140
	Epoxies, cold cured	Epikote (Epon), Araldite	EP	190
	Epoxies, hot cured	Epikote (Epon), Araldite	EP	150
Rubber/ elastomers	Natural rubber, soft	Linatex	NR	70
	Natural rubber, hard	Vulcoferran, Vulkodurit	NR	120
	Depolymerized rubber	–	–	90
	Polychloroprene	Neoprene, Baypren, Vulkodunit WR	CR	120
	Polyisoprene	Cariflex I	IR	80
	Polybutadiene styrene	Cariflex S, Buna SL, Hycar OS,GRS	SBR	120
	Polybutandiene acrylonitrile	Perbunan N, GRA, Buna N, Vulkodurit WT	NBR	120
	Polyisobutylene, isoprene	Butyl, GRI, Vulkodurit W50	IIR	140
	Vinylidene fluoride-chlorotrifluoroethylene	Kel-F elastomer	–	175
	Vinylidene fluoride hexafluoropropylene	Viton, Fluorel	FKM	230
	Polysulfides	Thlokol	–	60
	Silicon rubbers	Silastic, Rhocorsil, Silopren	SI	260
Ceramics/ carbonaceous materials	Carbon, non-impregnated	Durabon O/R		750
	Graphite, phenolic resin impregnated	Graphitor BS/HB, Vicarb VLA, Diabon N/NS		190
	Graphite, furane impregnated	Graphilor F, Vicarb VCG		190
	Acid resistant bricks/tiles			1300
	Stoneware			200
	Porcelain			250
	Glass			480
	Quartz/silica			1050
	Glass lined steel			225
	Fire-resistant bricks			1800
	Silicon carbide			1700
	Cement, Portland			300
	Cement, blast furnace			300
	Cement, alumina			300
	Cement, sodium silicate	Vitrex, Acalor 7, SWD		1000
	Cement, potassium silicate	Vitrex, Acalor 7K, HFR		1000
	Cement, phenolic	Asplit CN. Acalor 9		180
	Cement, furane	Asplit FN. Acalor 12, Furacin		180
	Cement, polyester	Asplit O		120
	Cement, epoxy	Asplit ET Wapex, Acalor 5		150
	Concrete (see cements)			300

Table 4.16 *(continued)*

Class	Chemical classification	Some trade names	Abbrev. (ASTM/BS/ DIN/ISO)	Max. working temp. (°C)
Paints/lacquers, hot cured, cold cured	Alkyd			60
	Vinyl			80
	Chlorinated rubber			70
	Epoxy, cold cured			120
	Epoxy, hot cured			120
	Phenolic			120
	Epoxy-phenolic			140

4.19 Composite Materials

There are very many situations in engineering where no single material will be suitable to meet a particular design requirement. However, two materials in combination may possess the desired properties, and provide a feasible solution to the material-selection problem. In this section some of the composites in current use will be mentioned.

4.19.1 Timber and Plywood

Plywood is built up of thin layers of wood bonded with a water-resistant glue or a thermosetting resin, with the grain of successive layers at right angles to each other.

4.19.2 Fiber-Reinforced Materials

High-strength fibers, such as glass, carbon, polymer, ceramics, and wire filaments, are encased within a tough matrix made up from thermoplastic and thermosetting resins, glasses, ceramics, and metals. Many different matrix/fiber combinations have been developed with different properties for different applications.

4.19.3 Sandwich Structures

The structures are generally composed of two skins of high strength with a lightweight core. This arrangement provides a material with low density and high specific stiffness, where the maximum tensile and compressive stresses are carried by the skin. These combinations also provide useful thermal and sound insulation. Skin materials include sheet metal, plywood, plastics, concrete and plasterboard, and cores may be metal or paper honeycomb structures, rigid plastic foam, chip board, or low-density porous masses of glass fiber or rockwool bonded with a plastic resin.

5

Chemical Control of Corrosive Environments

A corrosion inhibitor reduces the corrosion rate of a metal exposed to that environment. Inhibition is used internally with carbon steel pipes and vessels as an economic corrosion control alternative to stainless steels and alloys, coatings, or non-metallic composites, and can often be implemented without disrupting a process. The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment, and the product additive industries.

5.1 General Requirements and Rules for Corrosion Control

In the oil and gas industries, equipment will require replacement when:

- It has become fully out of service and non-operational.
- It no longer performs satisfactorily, although it still looks to be operational.
- Corrosion or other deterioration has made it unfit for further service.

According to the results of a failure analysis, certain corrective measures can be implemented. These include, for example, the use of alternative materials of construction, changes in equipment design and process conditions, application of protective coatings and linings, cathodic and anodic protection, and the use of corrosion inhibitors.

Process changes that can be considered for reducing corrosion and other failures include the following:

- Oxygen (air) can be removed by the use of scavenging chemicals.
- Temperature can be decreased to decrease corrosion rates.
- Water entry can be controlled by installation of calcium chloride drying equipment, settling drums, or demister screens.

Corrosion and Materials Selection: A Guide for the Chemical and Petroleum Industries, First Edition. Alireza Bahadori.
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- Concentrations of critical corrosive species can be adjusted.
- Flow velocity can be reduced to prevent erosion-corrosion

5.1.1 Corrosion Inhibitors

Corrosion inhibitors are usually categorised into various common types or mechanistic classes: passivating, vapor phase, cathodic, anodic, film-forming, neutralizing, and reactive. Inorganic inhibitors, such as disodium arsenite (Na_2HAsO_3) and ferrocyanide, have been used to inhibit carbon dioxide (CO_2) corrosion in oil wells, but the treatment frequency and effectiveness have not been satisfactory. This has led to the development of many organic chemical formulations that could almost be reduced to a single type of organic molecule: film-forming amines and their salts. These organic corrosion inhibitors can be classified as cathodic, anodic, or cathodic-anodic.

During the past 30 years, the primary improvements in inhibitor technology have been the refinement of formulations and the development of improved methods of applying inhibitors. The methods of evaluating the performance during their use have also advanced considerably. The best corrosion protection measures should be implemented on the basis of technical and economical aspects when establishing new constructions.

The consensus is that organic compounds inhibit corrosion by adsorbing at the metal/solution interface. Three possible types of adsorption are associated with organic inhibitors: π-bond orbital adsorption, electrostatic adsorption, and chemisorption. A more simplistic view of the mechanism of corrosion inhibitors can be described as controlled precipitation of the inhibitor from its environment (water and hydrocarbons) onto metal surfaces.

5.1.2 Types of Inhibitor

Inhibitors are usually grouped in six different classes as follows.

5.1.2.1 Organic Inhibitors

Organic inhibitors constitute a broad class of corrosive inhibitors that cannot be designated specifically as anodic, cathodic, or ohmic. As a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentrations.

5.1.2.2 Vapor-Phase Inhibitors

Vapor-phase inhibitors (VPIs), also called volatile corrosion inhibitors (VCIs) are compounds that are transported in a closed system to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or octadecylamine are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide. Compounds of this type inhibit corrosion by making the environment alkaline. In closed vapor spaces, such as shipping containers, volatile solids such as the nitrite, carbonate, and benzoate salts of dicyclohexylamine, cyclohexylamine, and hexamethyleneimine are used.

5.1.2.3 Anodic Inhibitors (Passivators)

There are two types of passivating inhibitors: oxidizing anions, such as chromate, nitrite, and nitrate, which can passivate steel in the absence of oxygen; and non-oxidizing ions, such as phosphate, tungstate, and molybdite, which require the presence of oxygen to passivate steel.

5.1.2.4 Ohmic Inhibitors

Ohmic inhibitors usually increase the ohmic resistance of the electrolyte circuit by the formation of a film on cathodic areas.

5.1.2.5 Cathodic Inhibitors

Cathodic inhibitors either slow the cathodic reaction itself, or they selectively precipitate on cathodic areas to increase circuit resistance and restrict diffusion of reducible species to the cathodes. Acid inhibitors such as arsenic and antimony compounds, and also oxygen scavengers are examples of cathodic inhibitors.

5.1.2.6 Precipitation-Inducing Inhibitors

These inhibitors are film-forming compounds that have a general action over the metal surface and that, therefore, interfere with both anodes and cathodes indirectly. The most common inhibitors of this class are the silicates and phosphates.

5.2 Basic Types of Inhibitors and How They Work

5.2.1 Polarization Diagrams

In this section, the relationship of corrosion inhibitors to anodic and cathodic polarization will be explained. Of the four components of a corrosion cell (anode, cathode, electrolyte, and electronic conductor), three may be affected by a corrosion inhibitor to retard corrosion. The inhibitor may cause:

- increased polarization of the anode (anodic inhibition)
- increased polarization of the cathode (cathodic inhibition)
- increase the electrical resistance of the circuit by forming a thick deposit on the surface of the metal.

Of course, the bulk film-formers also restrict diffusion of depolarizers (such as dissolved oxygen) to the surface of the metal; hence, they may play a dual role. The resistance of the electronic conductor connecting the anode and cathode (i.e. usually the resistance of the metal itself) is very low and cannot be changed by corrosion inhibitors.

The effects of a corrosion inhibitor on a corrosion cell are conveniently determined by polarizing the corroding metal in a suitable electrolyte with varying amounts of current from an external source such as a battery. A simple laboratory apparatus for polarization measurements is shown in Figure 5.1.

The force that must be applied to stimulate the anodic or cathodic reactions is measured by the potential difference between the working electrode and a reference electrode. No current is applied to the reference electrode; hence, it is used as a standard against which the potential of the working electrode is measured.

In an experiment to compare the effects of several inhibitors on the polarization of steel in a corrodent, such as dilute acid, the apparatus would be assembled using steel as the working electrode, dilute acid as the electrolyte, and an inert material such as carbon or platinum as an auxiliary electrode. Then the current would be increased in steps by means of a variable resistor, and the potential of the working electrode read at each step. A plot of current versus potential in the absence and presence of an inhibitor shows the effects of the inhibitor on the polarization characteristics of the steel.

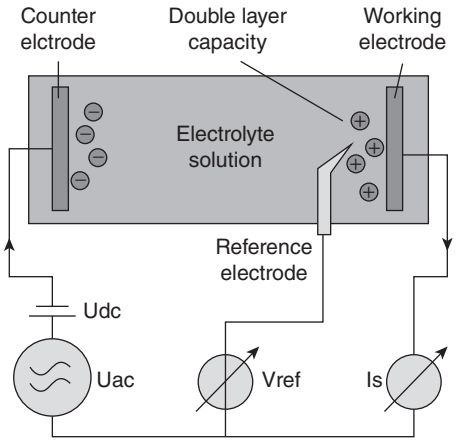


Figure 5.1 *Laboratory apparatus for polarization measurements.*

When no current is applied and the working electrode has achieved a steady state, then the potential is the corrosion potential, E_c, of the electrode material. The corrosion potential is the mixed potential to which the anodes and cathodes are polarized by the corrosion reaction. It is also an indication of the effects of corrosion inhibitors.

5.2.2 Types of Inhibitor

As mentioned earlier in this chapter, six classes of inhibitors will be discussed:

- Passivating (anodic)
- Cathodic
- Ohmic
- Organic
- Precipitation-inducing
- Vapor-phase.

While some authors may use slightly different classes, these will illustrate the complexity of the inhibitor picture.

5.2.2.1 Anodic Passivating Inhibitors

Anodic inhibition shows an increase in the polarization (a large potential change results from a small current flow) of the anode in the presence of an anodic inhibitor. Addition of the inhibitor causes the corrosion potential to shift in a cathodic direction.

Anodic inhibitors that cause a large shift in the corrosion potential are called passivating inhibitors. They are also called dangerous inhibitors because, if used in insufficient concentrations, they cause pitting and sometimes an increase in corrosion rate. There are two types of passivating inhibitors: oxidizing anions such as chromate, nitrite, and nitrate that can passivate steel in the absence of oxygen; and non-oxidizing ions such as phosphates, tungstate, and molybdate that require the presence of oxygen to passivate steel. With careful control, however, passivating inhibitors are frequently used because they are very effective in sufficient quantities. Passivating inhibitors such as sodium chromate (Na_2CrO_4) and sodium nitrite ($NaNO_2$) do not require oxygen to be effective. They increase the

rate of anodic passivation to the extent that the anodes are polarized to a passive potential (or Flade potential).

Note that when an insufficient amount of inhibitor is used, the cathodic curve will intersect the anodic curve in an active region or in both active and passive regions. In the former case, corrosion will proceed at a high rate; in the latter, passivity is unstable, and the corrosion potential will oscillate between both cases, usually resulting in pitting of the metal. Measurement of the corrosion potential when using passivators is a good way to determine if the inhibitor is doing its job, because a large positive shift in potential should occur if the metal passivates. Passivation by inhibitors is more difficult at higher temperatures, higher salt concentrations, lower pH, and lower dissolved oxygen concentrations.

5.2.2.2 Mechanism

The mechanism by which chromate passivates steel has been studied extensively, and it appears likely that protection is afforded by a combination of adsorption and oxide formation on the steel surface. Adsorption helps to polarize the anode to sufficient potentials to form very thin hydrated ferric oxides that protect the steel. Because the oxide film is invisible on steel, articles protected by chromate remain bright in otherwise aggressive environments. The oxide film is a mixture of ferric and chromic oxides and is kept in good repair by adsorption and oxidation, with very little loss of metal as long as sufficient chromate remains in solution.

Chromates are accelerators of corrosion at low concentration because they are good cathodic depolarizers. The passive oxide film is conductive and cathodic to steel; therefore passive steel consists almost entirely of cathodic areas. When the passive film is penetrated by scratching or by dissolution, and when insufficient chromate is present to repair the film, the exposed steel becomes a small anodic area in which accelerated localized corrosion can occur, resulting in pitting of the metal. Mechanisms similar to that proposed for chromate are believed to apply to nitrites and nitrates.

It is practical to passivate steel in any aqueous solution, except those containing easily oxidized substances in solution or high concentrations of chloride ions. For example, chromate should not be used in hydrogen sulfide, (H_2S)-containing (or sour) environments because it is lost by oxidation of the sulfide to free sulfur. High concentrations of chloride ions prevent passivation because they compete with chromate for adsorption, thus preventing polarization of the anodes. They also prevent deposition oxides by forming a soluble complex with ferric ions.

For a given concentration of passivating inhibitor, there is a concentration of chloride and sulfate ions that will cause depassivation. Table 5.1 lists the "critical concentrations" of sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) required to cause pitting of steel in the presence of various

Table 5.1 *Critical concentration of sodium chloride or sodium sulfate above which pitting of Armco iron occurs in chromate or nitrite solutions*

Inhibitor	Concentration, ppm	Critical concentration, ppm	
		NaCl	Na_2SO_4
Na_2CrO_4	200	12	25
	500	30	120
$NaNO_2$	50	210	20
	100	460	55
	500	1000	450

Five-day tests, 25 °C, stagnant solutions
Source: H.H. Uhlig, Corrosion and Corrosion Control, John Wiley & Sons, Inc., New York, NY, P.232 (1963).

Table 5.2 *Amount of sodium chromate consumed by steel in 50 days in establishing passivity in sodium chloride solutions*

Sodium chromate ppm	Sodium chromate consumed in water containing kg/1000 m^2 (lb/1000 sq ft)	
	10 ppm NaCl	1000 ppm NaCl
25	4.88 (1)	–
50	6.35 (1.3)	–
100	2.44 (0.5)	5.37 (1.1)
250	1.46 (0.3)	6.35 (1.3)
500	0.49 (0.1)	3.42 (0.7)
1000	0.49 (0.1)	3.42 (0.7)

Source: M. Darrin. Ind. Eng. Chem. Vol. 38, p. 368 (1946).

concentrations of sodium chromate and sodium nitrite. The critical concentrations will vary, depending on other factors; for example, more chloride or sulfate will be required for depassivation as the temperature is lowered, the oxygen concentration is increased, or the pH is increased.

Chromate concentration should be maintained at a level at least twice that required to prevent pitting. In calculating the amount of chromate needed for passivation, allowance should be made for the inhibitor, which is consumed initially in establishing the passive film.

The amount of sodium chromate consumed in passivating steel in sodium chloride solutions is given in Table 5.2. For example, if it is desired to maintain 250 ppm of sodium chromate in water containing 1000 ppm of sodium chloride, then, referring to Table 5.2, 6.35 kg of sodium chromate per thousand square meters of exposed steel should be added in addition to the quantity required to achieve a concentration of 250 ppm.

Non-oxidizing passivators such as sodium benzoate, polyphosphate, and sodium cinnamate require the presence of oxygen to cause passivation. They do not inhibit corrosion in the absence of oxygen. They apparently function by promoting the adsorption of oxygen on the anodes, thereby causing polarization into the passive region. Non-oxidizing passivators are also dangerous when used in insufficient amounts because the oxygen required for passivation is a good cathodic depolarizer.

5.2.2.3 Cathodic Inhibitors

Cathodic inhibitors either slow the cathodic reaction itself, or they selectively precipitate on cathodic areas to increase circuit resistance and restrict diffusion of reducible species to the cathodes.

The cathodic reaction is often the reduction of hydrogen ions to form hydrogen gas. Some cathodic inhibitors make the discharge of hydrogen gas more difficult, and they are said to increase the hydrogen overvoltage. Compounds of arsenic and antimony are examples of this type of inhibitor that are often used in acids or in systems where oxygen is excluded. Another possible cathodic reaction is the reduction of oxygen. The inhibitors for this cathodic reaction are different from those mentioned for more acidic systems.

Other cathodic inhibitors utilize the increase in alkalinity at cathodic sites to precipitate insoluble compounds on the metal surface. The cathodic reaction, hydrogen ion and/or oxygen reduction, causes the environment immediately adjacent to the cathodes to become alkaline; therefore, ions such as calcium, zinc, or magnesium may be precipitated as oxides to form a protective layer on the metal. Many natural waters are self-inhibiting due to the deposition of a scale on metals by precipitation of naturally occurring ions. Inhibition by polarization of the cathodic reaction can be achieved in several ways, and several examples have already been given. The three main categories of inhibitors that affect cathodic reaction are cathodic poisons, cathodic precipitates, and oxygen scavengers.

5.2.2.4 Cathodic Poisons

Cathodic poisons are substances that interfere with the cathodic reduction reactions, i.e., hydrogen atom formation and hydrogen gas evolution. The rate of the cathodic reaction is slowed, and because anodic and cathodic reactions must proceed at the same rate, the whole corrosion process is slowed.

While some cathodic poisons such as sulfides and selenides are adsorbed on the metal surface, compounds of arsenic, bismuth, and antimony are reduced at the cathode to deposit a layer of the respective metals. Sulfides and selenides generally are not useful inhibitors because they are not very soluble in acidic solutions, they precipitate many metal ions, and they are toxic. Arsenates are used to inhibit corrosion in strong acids, but in recent years the trend has been to rely more on organic inhibitors because of the toxicity of arsenic.

A serious drawback to the use of cathodic poisons is that they sometimes cause hydrogen blistering of steel and increase its susceptibility to hydrogen embrittlement. Since the recombination of hydrogen atoms is inhibited, surface concentration of hydrogen atoms is increased, and a greater fraction of the hydrogen produced by the corrosion reaction is adsorbed into the steel. Note that hydrogen is adsorbed on the surface, but some of it is absorbed into the steel. Hydrogen atoms that penetrate the steel may pass through and diffuse out the other side if it also is not corroding to produce hydrogen. Blisters are formed when hydrogen atoms combine to form hydrogen molecules (H_2) inside the steel. Molecular hydrogen does not diffuse through steel; therefore, it collects at defects or voids to create pressures that may reach a million psi or more. Only small amounts of sulfide or arsenic are required to increase the amount of hydrogen penetrating the steel, which accounts for the frequent occurrence of blistering and hydrogen embrittlement in the presence of these poisons.

It has been suggested that the adsorption of hydrogen by steel could be used to advantage in sealed absorption-type refrigeration machines. Corrosion occurs very slowly in these systems, but sufficient hydrogen is produced to lower the efficiency of the thermal cycle, thus requiring an occasional pump-down of the units. The use of an inhibitor, such as an antimony compound, would cause the hydrogen to pass through the steel piping and vessels so that pumping would not be required. In this application, it would be important to use a steel that is not susceptible to blistering or embrittlement.

5.2.2.5 Cathodic Precipitates

The most widely used cathodic precipitation-type inhibitors are the carbonates of calcium and magnesium because they occur in natural waters and their use as an inhibitor usually requires only an adjustment of pH. Zinc sulfate ($ZnSO_4$) precipitates as zinc hydroxide $Zn(OH)_2$ on cathodic areas and is considered an inhibitor of this type. Phosphates and silicates are not distinctively cathodic or anodic inhibitors, but appear to be a combination of both types, so they will be considered later in the section on precipitation inhibitors.

Many natural waters and municipal water supplies contain calcium carbonate (limestone, $CaCO_3$) in solution. Limestone is dissolved in water to form soluble calcium bicarbonate ($Ca(HCO_3)_2$). Limestone can be caused to precipitate again, forming a milky-white suspension, by making the calcium bicarbonate solution more alkaline or by adding more calcium. Usually, lime is added to accomplish both objectives.

The objective of corrosion-inhibiting water treatment is to increase the alkalinity of the water to a pH at which precipitation of $CaCO_3$ is just about to occur. If the appropriate pH is exceeded, $CaCO_3$ will precipitate to form a slimy, porous deposit that does not provide corrosion protection and may increase corrosion by creating concentration cells involving oxygen. At the correct pH, the deposit will be fairly hard and smooth, similar to an eggshell. Once a protective deposit is formed, the pH of the water must be maintained at the equilibrium level, because if it is allowed to become acidic, the protective layer will redissolve.

A convenient way to express the condition of water with respect to its tendency to deposit $CaCO_3$ is the Langelier Index, which is the difference between the pH of the water and the pH required to precipitate $CaCO_3$.

Although many metal ions form insoluble hydroxides, few are useful cathodic corrosion inhibitors. Zinc sulfate, which is a good example, when added to neutral water, causes polarization of the cathodic reaction by precipitating zinc hydroxide.

5.2.2.6 Oxygen Scavengers

Corrosion of steel in water above about pH 6.0 is due to the presence of dissolved oxygen, which depolarizes the cathodic reaction and increases corrosion. Neutral water of low salt content in equilibrium with air at 21 °C (70 °F) will contain about 8 ppm of dissolved oxygen. The concentration of oxygen decreases with increasing salt concentration and increasing temperature. Only 0.1 ppm of oxygen is required to increase corrosion rates seriously in a dynamic system.

In static systems, a higher concentration of oxygen is required to increase the corrosion rate seriously because the corrosion reaction soon depletes the oxygen supply in the immediate vicinity of the metal. Oxygen scavengers help inhibit corrosion by preventing cathodic depolarization caused by oxygen. Oxygen scavengers are added to water, either alone or with a corrosion inhibitor, to retard corrosion. Organic corrosion inhibitors alone in aerated brine water will slow general corrosion, but will not always prevent pitting attack. The most common oxygen scavengers used in water at ambient temperatures are sodium sulfite (Na_2SO_3) and sulfur dioxide (SO_2). At elevated temperatures, hydrazine is used to remove oxygen.

The reaction rate of sulfites with oxygen at low temperature is slow, so a catalyst is usually added, the best being cobalt, manganese, and copper salts. Cobalt gives the greatest increase in reaction rate. Copper should not be added to water that contacts steel or aluminum because it lowers the hydrogen overvoltage and increases the corrosion rate.

Consequently, cobalt is preferred and manganese is a close second. Hydrazine reacts very slowly with oxygen in water at low temperatures in the absence of a catalyst, and thus is not often used at low temperatures. The hazards of hydrazine are significant, especially in the hands of untrained personnel. In high-pressure boilers, hydrazine is the preferred oxygen scavenger.

Figures 5.2 and 5.3 show the effect of hydrogen sulfide on ammonium bisulfite when used as an oxygen scavenger in aqueous solutions.

5.2.2.7 Ohmic Inhibitors

Inhibitors that increase the ohmic resistance of the electrolyte circuit have already been considered to some extent in the sections on anodic and cathodic film-forming inhibitors. Because it is usually impractical to increase resistance of the bulk electrolyte, increased resistance is practically achieved by the formation of a film, a micro-inch thick or more, on the metal surface.

If the film is deposited selectively on anodic areas, the corrosion potential shifts to more positive values; if it is deposited on cathodic areas, the shift is to more negative values; and if the film covers both anodic and cathodic areas, there may be only a slight shift in either direction.

5.2.2.8 Organic Inhibitors

Organic compounds constitute a broad class of corrosion inhibitors that cannot be designated specifically as anodic, cathodic, or ohmic. Anodic or cathodic effects alone are sometimes observed in the presence of organic inhibitors, but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Probably both anodic and cathodic areas are inhibited, but to varying degrees, depending on the potential of the metal, the chemical structure of the inhibitor molecule, and the size of the molecule.

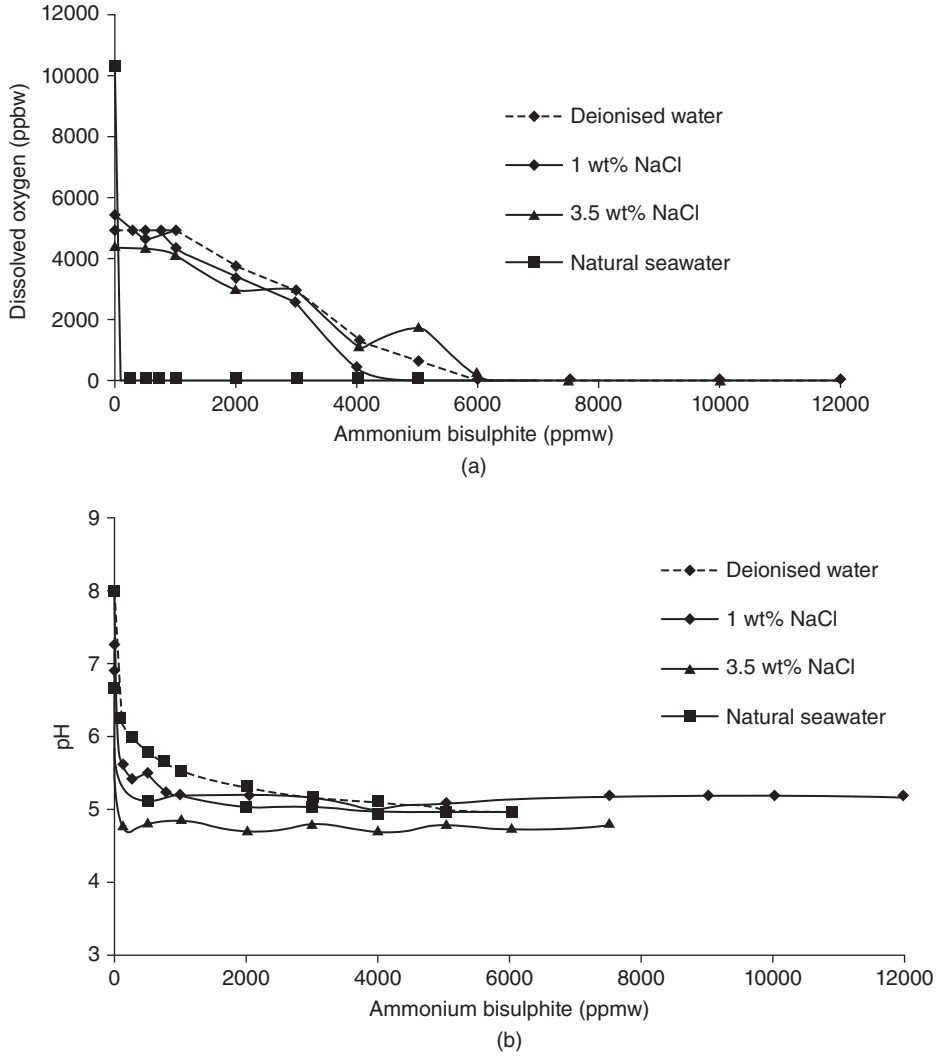


Figure 5.2 *Effect of ammonium bisulphite (ABS) concentration on (a) dissolved oxygen level and (b) pH, for all the test solutions. (Reprinted from Lasebikan* et al.*, 2011, with permission from Elsevier.)*

The typical increase in corrosion inhibition with inhibitor concentration, suggests that inhibition is the result of adsorption of inhibitor on the metal surface. The film formed by adsorption of soluble organic inhibitors is only a few molecules thick and is invisible.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the metal surface. Cationic inhibitors (positively charged, +), such as amines, or anionic inhibitors (negatively charged, −), such as sulfonates, will be adsorbed preferentially, depending on whether the metal is charged negatively or positively (opposite sign charges attract). The in-between potential at which neither cationic nor anionic molecules are preferred is known as the zero point of charge or ZPC. Thus, a combination of cathodic protection and an inhibitor that is adsorbed more strongly at negative potentials gives greater inhibition than either cathodic protection or an inhibitor alone.

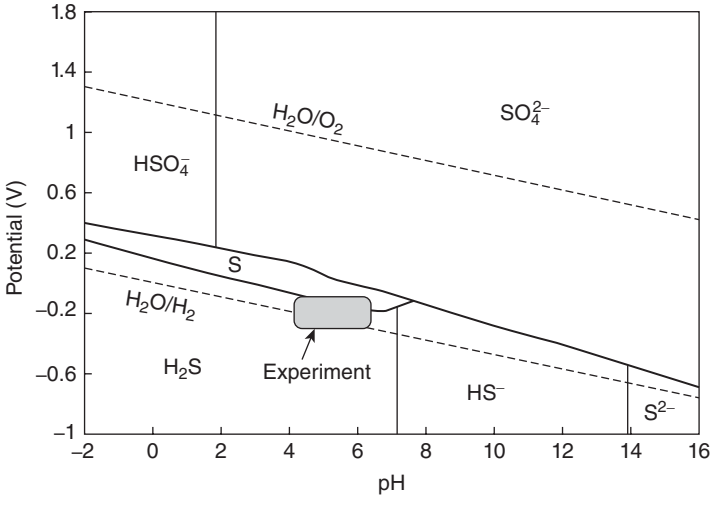


Figure 5.3 *Pourbaix EH–pH diagram for sulfur–water system at 25°C and 1 atm. The shaded region represents experimental measurements for the test solutions: 3.5 wt.% NaCl + 1000 ppmw ABS, 1 wt.% NaCl + 1000 ppmw ABS, 3.5 wt.% NaCl + 500 ppmw ABS, deionized water + 1000 ppmw ABS, and 1 wt.%NaCl + 500 ppmw ABS. (Reprinted from Lasebikan* et al.*, 2011, with permission from Elsevier.)*

5.2.2.9 Synergy with Halogen Ions

The efficiency of organic amines as corrosion inhibitors is improved when certain halogen ions are present. Halogen ions alone inhibit corrosion to some extent in acid solutions. The iodide (I^-) ion is the most effective, followed by bromide (Br^-) and chloride (Cl^-). Fluoride (F^-) does not have significant inhibitive properties. Chloride ions, for example, lower the rate of attack on steel by sulfuric acid. A combination of amine and iodide may be more inhibitive than either additive alone, i.e., the two additives are synergistic.

One explanation for synergism is that steel adsorbs iodide ions whose charge shifts the surface potential in a negative direction, thereby increasing adsorption of the cationic amine.

5.2.2.10 Effects of Molecular Structure

How the size of organic molecules influences their effectiveness as corrosion inhibitors has been investigated many times. However, the results are not consistent enough to permit formulation of a general rule regarding the effect of increasing molecular weight.

Primary amines, such as *n*-decylamine, become more efficient inhibitors as the chain length is increased, but, in contrast, primary aliphatic mercaptans, such as *n*-butyl mercaptan and some aldehydes, decrease in efficiency as the chain length is increased.

These results are probably due to the interaction of various factors that influence the strength of the adsorption bond, the compactness of the adsorbed layer, and tendency of the adsorbed molecules to cross link or otherwise interact with neighboring molecules.

There is little doubt that the bonding of amines to a metal surface is through the nitrogen atom. For example, in the series of saturated cyclic imines, inhibitor efficiency increases as the number of carbon atoms in the ring is increased up to at least 10.

5.2.2.11 Adsorption

The observations given previously indicate that for soluble organic inhibitors, the strength of the adsorption bond is the dominant factor. Adsorption of an inhibitor from solution establishes the following equilibrium:

$$I_{solution} \leftrightarrow I_{surface} \tag{5.1}$$

where I is the concentration of a soluble organic inhibitor.

It is characteristic of an equilibrium that if the concentration of one species is changed, then the concentration of species with which it is in balance will change in the same direction to preserve equilibrium. From the above equation, it can be seen that the amount of inhibitor on the surface increases with the amount in solution, i.e., the concentration of inhibitor used in the environment to be inhibited. Inhibitor efficiency increases with concentration until the surface is saturated, i.e. it has adsorbed inhibitor molecules on all available sites.

Therefore, the stronger the adsorption bond, the lower the concentration of inhibitor in solution required to achieve a given coverage of the surface. Soluble organic inhibitors form a protective layer only a few molecules thick, but if an insoluble organic inhibitor is added by dispersion as fine droplets, the film may continue to build to a thickness of several thousandths of an inch.

Such films show good persistence, i.e. they continue to inhibit corrosion for a time after an inhibitor is no longer injected into the environment. Persistency is an important property when inhibitors can be injected into a system only in portions.

5.2.2.12 Precipitation Inhibitors

Precipitate-inducing inhibitors are film-forming compounds that have a general action over the metal surface and therefore interfere with both anodes and cathodes indirectly. The most common inhibitors of this class are the silicates and phosphates.

In water with a pH near 7.0, a low concentration of chlorides, silicates, and phosphates cause passivation of steel when oxygen is present; hence, they behave as anodic inhibitors. Another anodic characteristic is that corrosion is localized in the form of pitting when insufficient amounts of phosphate or silicate are added to saline water. However, both silicates and phosphates from deposits on steel increase cathodic polarization. Thus, their action appears to be mixed, i.e., a combination of both anodic and cathodic effects.

Silicate is used most often in low salinity water containing oxygen. It has the rare property of inhibiting the corrosion of steel that is already scaled with rust. While the concentration of silicate required for protection depends on the salinity of the water, for most city water supplies, 5 to 10 ppm are required initially, followed by a gradual reduction to 2 to 3 ppm after a protective deposit is established. High concentrations of calcium and magnesium interfere with inhibition by silicates, but this problem is often overcome by adding 2 to 3 ppm of polyphosphates in addition to the silicates.

Sodium silicate is used in many private water softeners to prevent the occurrence of red water or rust water, which is caused by suspended ferric hydroxide. The silicates remove iron by precipitation, so they should not be used where formation of scales cannot be tolerated.

In aerated hot water systems, sodium silicate protects steel, copper, and brass. However, protection is not always reliable and depends on the pH and composition of the water. The best procedure is to adjust the saturation index, as already described to facilitate formation of a protective silicate-containing film.

Phosphates, like silicates, require oxygen for effective inhibition. A concentration of sodium hexametaphosphate, a typical polyphosphate, of about 10 ppm provides corrosion inhibition in aerated

water if the water is in motion. In stagnant areas, corrosion might be increased due to the establishment of oxygen concentration cells.

In addition to motion, the presence of calcium ions is essential to inhibition. Phosphates inhibit the deposition of $CaCO_3$; therefore, the concentration of phosphate and calcium must be in proper balance to obtain effective inhibition.

A rule of thumb is that the phosphate must not exceed twice the concentration of calcium carbonate. Therefore, if the water contains 10 ppm of calcium carbonate, then up to 20 ppm of phosphate can be used for inhibition. If the water is exceedingly soft, calcium can be increased by the addition of lime.

If chromate cannot be used because windage losses or disposal cause problems due to the toxicity of chromate, industrial cooling towers can be inhibited with about 50 ppm of sodium hexametaphosphate. Addition of a soluble zinc salt often improves inhibition by polyphosphates. Pitting and excessive scale formation are prevented by maintaining the pH in a range 6 to 7.

The silicates and phosphates do not afford the degree of protection that can be obtained with chromates and nitrites; however, they are very useful in situations where non-toxic additives are required. Their main drawbacks are their dependence on water composition and the careful control required to achieve maximum inhibition.

5.2.2.13 Vapor-Phase Inhibitors

Vapor-phase inhibitors (VPIs), also called volatile corrosion inhibitors (VCIs), are compounds which are transported in a closed system to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or octadecylamine are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide. Corrosion inhibitor compounds vaporize from the paper or film. They are attracted to the charged surface of the metal by virtue of their polar orientation.

The VCI molecules align on the surface of the metal to a depth of three to five molecules. This layer of molecules passivates the charged surface and creates a barrier that prevents oxidation. The corrosion cell (the flow of electrons in the metal and the flow of ions in the electrolytic surface layer) is unable to establish itself and corrosion is halted. The VCI molecules migrate into recesses and hard to reach areas on even the most complex shapes. The molecules build up on the metal surface until a continuous barrier has formed on the metal part (see Figure 5.4).

Compounds of this type inhibit corrosion by making the environment alkaline. In a closed vapor space, such as a shipping container, volatile solids such as the nitrite, carbonate, and benzonate salts of dicyclohexylamine, cyclohexylamine, and hexamethylene-imine are used. The mechanism of inhibition by these compounds is not entirely clear, but it appears certain that the organic portion of the molecules merely provides volatility.

On contact with a metal surface, the inhibitor vapor condenses and is hydrolyzed by any moisture present to liberate nitrite, benzoate, or bicarbonate ions. Since ample oxygen is present, nitrite, and benzoate ions are capable of passivating steel as they do in aqueous solution. The mechanism for carbonate may not be the same, and here the organic amine portion of the VPI may serve to aid inhibition by adsorption and by providing alkalinity.

It is desirable for a VPI to provide inhibition rapidly and to have a lasting effect. Therefore, the compound should have a high volatility to saturate all of the accessible vapor space as quickly as possible, but at the same time it should not be too volatile, because it would be lost rapidly through any leaks in the package or container in which it is used. The optimum vapor pressure of VPI then would be just sufficient to maintain an inhibiting concentration on all exposed metal surfaces. Vapor pressures and other properties of some VPIs are given in Table 5.3.

Note that the vapor pressure of cyclohexylamine carbonate is 2000 times higher than dicyclohexylamine nitrite, thus making it a better choice for containers that are opened occasionally because it will resaturate the vapor space rapidly. Dicyclohexylamine nitrite is advantageous for once-opened containers that may be stored for extended periods. The amount of VPI required depends on conditions,

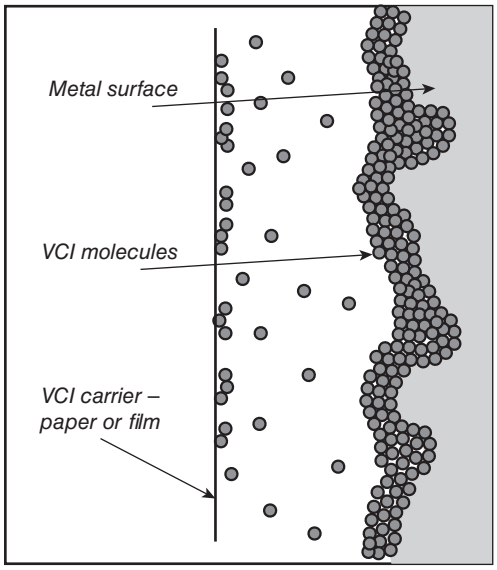


Figure 5.4 *The molecules build up on the metal surface until a continuous barrier has formed on the metal part. (Reproduced with permission from Daubert Cromwell.)*

Table 5.3 *Properties of vapor-phase inhibitors*

Compound	Vapor pressure mmHg at 25 °C	Remarks
Dicyclohexylamine nitrite	0.0002	Protects steel, aluminum, and tinplate. Increases corrosion of zinc, magnesium, cadmium, lead, and copper. Discolors some plastics.
Cyclohexylamine carbonate	0.4	Protects steel, aluminum, solder, tin, and size. No effect on cadmium. Increases corrosion of copper, brass, and magnesium.

but 2.2 kg per 100 m^2 (1 lb per 500 ft^2) of surface has been suggested for dicyclohexylamine nitrite and 2.2 kg per 30 m^3 (1 lb per 500 ft^3) of space for cyclohexyalmine carbonate.

Vapor-phase inhibitors attack non-ferrous metals to varying degrees, so it is suggested that a potential user test several of the commercially available VPIs for the particular application. Compatibility of the amines and nitrites with any copper alloys should especially be considered.

5.3 Corrosive Environments

Corrosive environments to which corrosion inhibitors apply are as follows.

5.3.1 Aqueous Systems

Aqueous systems are by far the most common environments to which corrosion inhibitors are applied. Water is a powerful solvent capable of carrying many different ions at the same time, so requirements

for corrosion inhibition may vary greatly, depending on the type and amount of dissolved species present. Because there is no universal inhibitor for water systems, an inhibitor that may be satisfactory for one system may be ineffective or even harmful in another.

The main factors that may be considered in the application of corrosion inhibitors to aqueous systems are salt concentration, pH, dissolved oxygen concentration, and the concentrations of interfering species.

5.3.2 Strong Acids

High acid concentrations are encountered in pickling processes, oil-well acidizing, and during the transportation of acids for use in chemical processes. Hydrochloric acid of all concentrations requires an inhibitor if steel is to be used. The use of an inhibitor in pickling processes also allows the acid to dissolve scale from steel without appreciable attack on the metal.

5.3.3 Non-Aqueous Systems

Corrosion in non-aqueous liquids such as fuels, lubricants, and edible oils is usually caused by the small amounts of water often present. Water is slightly soluble in petroleum products, and its solubility increases with temperature. If a non-aqueous solvent is saturated with water and the temperature is lowered, then some of the water will separate out to attack any steel that it contacts.

Oil that has been subjected to high temperatures in air will contain organic acid that will be extracted by any water present to increase the rate of attack on the steel. Corrosion in steel systems handling wet oils can be inhibited with both organic and inorganic compounds. Effective organic compounds include various amines, lecithin, and mercaptobenzothiazole. The inorganic inhibitors include sodium nitrite and sodium nitrate. Chromates are not used because of their instability in the presence of organics.

Small amounts of water inhibit corrosion in some non-aqueous solvents. Halogenated (containing chlorides, fluorides, bromides, or iodides), non-aqueous solvents can be particularly troublesome. Organic amines are effective inhibitors for steel degreasing vessels that contain hot chlorinated solvents.

5.3.4 Gaseous Environments

Gaseous environments include the open atmosphere, the vapor phase in tanks, natural gas in wells, and the empty space in packaging containers. Here again, water and oxygen are the principal corrosive agents, but the main problem in providing inhibition is to transport the inhibitor from the source to the sites where corrosion may occur.

5.3.5 Effect of Elevated Temperatures

Most effects of elevated temperatures are detrimental to corrosion inhibition. High temperatures increase corrosion rates (about double for a 15 °C rise at room temperature), and they decrease the tendency of inhibitors to adsorb onto metal surfaces. Precipitate-inducing inhibitors are less effective at elevated temperatures because of the greater solubility of the protective deposit.

Thermal stability of corrosion inhibitors is an important consideration at high temperatures. Polyphosphates, for example, are hydrolyzed by hot water to form orthophosphates, which have little inhibitive value. Most organic compounds are unstable above about 200 °C, hence they may provide only temporary inhibition at best.

5.4 Techniques for the Application of Inhibitors

5.4.1 Continuous Injection

Continuous injection of corrosion inhibitors is practiced in once-through systems where portions or batch treatment cannot be distributed evenly through the fluid. This method is used for water supplies, oil-field injection water, once-through cooling water, open annulus oil or gas wells, and gas lift wells. Liquid inhibitors are injected with a chemical injection pump. These pumps are extremely reliable and require little maintenance. Most chemical injection pumps can be adjusted to deliver the desired injection rate.

Another form of continuous application is by the use of slightly soluble forms of solid inhibitors. The inhibitor (such as glassy phosphate or silicate in the form of a cartridge) is installed in a flow line where it is continuously leached out by passage of fluid through the cartridge. Inhibitors in the form of sticks or pellets are used in oil and gas wells to supply inhibitor continuously by their natural slow dissolution.

Boilers, closed cooling water systems, and other closed circulating fluid systems can be treated with inhibitors with continuous injection. When such systems are started up after construction or major maintenance, the inhibitor is often injected at higher-than-normal concentration to permit rapid development of protective films.

5.4.2 Batch Treatment

The most familiar example of batch treatment is the automobile cooling system. A quantity of inhibitor is added at one time to provide protection for an extended period. Additional inhibitor may be added periodically, or the fluid may be drained and replaced with a new supply. In most aerated, closed-loop cooling systems, it is important that the inhibitor concentration be measured occasionally to ensure that a safe level is maintained.

Batch treatment is also used in treating oil and gas wells. An inhibitor is diluted with an appropriate solvent and injected into the annulus of open-hole wells or into the tubing of gas wells that have a packer. In this application, it is important that the inhibitor contacts all surfaces and that it has good persistence. Most wells require treatment about every two weeks.

5.4.3 Squeeze Treatment

The squeeze treatment is a method of continuously feeding an inhibitor into oil or gas wells. A quantity of inhibitor is pumped into a well and is followed by sufficient solvent to force the inhibitor into the formation, or inhibitor is mixed in oil, aromatic solvent, or water at the proper ratio, pumped into the tubing and displaced to the bottom, followed by sufficient fluid to overdisplace the mixture into the formation by 3500 to 11 500 liters. The inhibitor is absorbed by the formation, from which it slowly escapes to inhibit the produced fluids. Protection applied in this manner has been known to last for a year.

5.4.4 Volatilization

Volatilization has already been discussed under vapor phase inhibitors in connection with boilers and closed containers. Another application is the inhibition of gas condensate corrosion. However, the treatment here is essentially the same as used in batch or squeeze treatments.

5.4.5 Coatings

Inhibitors are used in coatings exposed to the open atmosphere. When moisture contacts the paint, some inhibitor is leached out to protect the metal. Thus, the inhibitor must be soluble enough to be leached out in sufficient amounts to protect the metal, but not so soluble that it will be lost rapidly.

The most common coating inhibitors are zinc chromate and plumbous orthoplumbate (red lead), which passivate steel by providing chromate and plumbate ions, respectively, as well as zinc and lead cathodic inhibitors. These inhibitors are not effective against attack by seawater or brine because the high chloride concentration prevents the passivation of steel.

Recently, heavy coatings, which act as sealants for crevices, have been developed for the aircraft and aerospace industries. These coatings contain proprietary inhibitor formulations that are especially effective in minimizing corrosion associated with dissimilar metal fasteners.

5.5 Inhibitor Mechanisms

5.5.1 Neutralizing Inhibitors

Neutralizing inhibitors lessen the corrosivity of the environment by decreasing hydrogen ion (H^+) concentration, which reduces the concentration of the corrosive reactant. Neutralizers function by controlling the corrosion caused by acidic materials, such as hydrogen chloride, carbon dioxide (CO_2), sulfur dioxide (SO_2), carboxylic acids, and related compounds. These materials are found in small quantities in many process streams.

However, because of such separation processes as distillation, one or more of these acidic species can concentrate in specific areas and cause severe corrosion. The area most susceptible to corrosion in the refinery is the heat exchanger, where the first drops of water condense (the initial condensate). An effective neutralizer will exhibit the same distillation/condensation properties as the acid is designed to control.

A variety of neutralizers are used in many applications in the refinery. The list includes ammonia (NH_3), and various proprietary alkylamines and polyamines. The physical characteristics of each neutralizer determine its application. A strong alkali, such as NaOH, is an excellent neutralizer when injected into desalted crude, but it cannot be used in overhead heat exchangers. Ammonia is an inexpensive overhead neutralizer, but it has no solubility in the initial condensate.

5.5.2 Filming Inhibitors

Most inhibitors used are of the film-forming type. Instead of reacting with or removing an active corrodent species, filming inhibitors function by creating a barrier between the metal and the environment. They consist of one or more polar groups based on nitrogen, sulfur, or oxygen that are attached to the metal surface by chemisorption or electrostatic forces.

Filming amine chemistry in the refinery includes amides, diamides and imidazoline salts. Each type is known to be effective in selected environments. The amino group is the important functional and salt-forming species. For readily handled commercial products, the amide intermediate is reacted with an imidazoline salt to enhance solubility in carrier solvents and to decrease gelling or phase separation. However, both groups are effective inhibitors.

5.5.3 Scavengers

Perhaps the most widely used scavenger system is employed in boilers to remove oxygen from the feed water. Techniques such as steam stripping can be used to remove most of the dissolved oxygen

from water; however, such methods become increasingly costly when the last traces of oxygen must be removed from the boiler feed water. In these cases, chemical techniques for oxygen removal become more attractive. Hydrazine and sodium sulfite are the two most widely used scavengers in boiler systems.

5.5.4 Miscellaneous Inhibitors

Miscellaneous inhibitors include such materials as scale inhibitors, which minimize deposition of scale on the metal surface, and biocides, which kill living organisms that can foul equipment.

5.6 Criteria for Corrosion Control by Inhibitors

The use of corrosion inhibitors has grown to be one of the foremost methods of combating corrosion. To use them effectively, the corrosion engineer must, first of all, be able to identify those problems that can be solved by the use of corrosion inhibitors. Second, the economics involved must be considered, i.e. whether or not the loss due to corrosion exceeds the cost of the inhibitor and the maintenance and operation of the attendant injection system. Third, the compatibility of inhibitors with the process being used must be considered to avoid adverse effects such as foaming, decrease in catalytic activity, degradation of another material, loss of heat transfer, etc. Finally, the inhibitor must be applied under conditions that produce maximum effect. Similar criteria should be used when combating the scale problems alone.

5.7 System Condition

A system must be carefully examined before a program of corrosion inhibition can be planned effectively. The examination must include a survey of any adverse effects an inhibitor may have on the process in which it is to be used and an analysis to detect the presence of interfering substances.

Another possible adverse effect of inhibition is an increased rate of corrosion of a metal in the system other than the one the the inhibitor was selected to protect. For example, some amines protect steel admirably, but will severely attack copper and brass. Nitrites may attack lead and lead alloys such as solder.

In some cases, the inhibitor may react in the system to produce a harmful product. An illustration of this is the reduction of nitrite inhibitors to form ammonia, which causes stress corrosion cracking of copper and brass. The only way to avoid these problems is to know the metallic components of a system and be thoroughly familiar with the properties of the inhibitor to be used (see Tables 5.4 and 5.5).

The examination must include preparation of a complete list of materials, both metallic and nonmetallic, that will be in contact with the fluid to be inhibited. Such small items as gaskets, instrument probes, and control devices may be made from materials that will not be compatible with some inhibitors. The results from this examination may suggest that certain parts of a system should be changed to permit the use of a particular inhibitor.

The examination must also include a determination of the cleanliness of the surfaces of the system that will be in contact with the inhibited fluid. A system can be plugged as the result of an inhibitor loosening scale and suspending it in the fluid. This problem is best avoided by planning ahead. The best preventive measure is to clean the system thoroughly, if possible, before an inhibitor is applied.

Table 5.4 *Some corrosive systems and the inhibitors that have been used to protect them*

System	Inhibitor	Metals protected	Concentration
Water, potable	$Ca(HCO_3)_2$	Steel, cast iron + others	10 ppm
	Polyphosphate	Fe, Zn, Cu,Al	5–10 ppm
	$Ca(OH)_2$	Fe, Zn, Cu	Sufficient for pH 8.0
	Na_2SiO_3	Fe, Zn, Cu	10–20 ppm
Water, cooling	$Ca(HCO_3)_2$	Steel, cast iron + others	10 ppm
	Na_2CrO_4	Fe, Zn, Cu	0.1%
	$NaNO_2$	Fe	0.05%
	NaH_2PO_4	Fe	1%
	Morpholine	Fe	0.2%
Boilers	NaH_2PO_4	Fe, Zn, Cu	10 ppm
	Polyphosphate	Fe, Zn, Cu	10 ppm
	Morpholine	Fe	Variable
	Hydrazine	Fe	O2 Scavenger
	Ammonia	Fe	Neutralizer
	Octadecylamine	Fe	Variable
Brines	$Ca(HCO_3)_2$	Fe, Cu, Zn	10 ppm
	Na_2CrO_4	Fe, Cu, Zn	0.1%
	Sodium benzoate	Fe	0.5%
	$NaNO_2$	Fe	(NaCl 5%)
Oil-field brines	Na_2SiO_3	Fe	0.01%
	Na_2SO_3(or SO_2)	Fe	O_2 scavenger ($O_2 \times 9$) ppm
	Quaternaries	Fe	10–25 ppm
	Imidazoline	Fe	10–25 ppm
	Rosin amine acetate	Fe	5–25 ppm
	Coco amine acetate	Fe	5–15 ppm
	Formaldehyde	Fe	50–100 ppm
Seawater	Na_2SiO_3	Zn	10 ppm
	$NaNO_2$	Fe	0.5%
	$Ca(HCO_3)_2$	All	pH Dependent
	$NaH_2PO_4 + NaNO_2$	Fe	10 ppm + 0.5%
Engine coolants	Na_2CrO_4	Fe, Pb, Cu, Zn	0.1–1%
	$NaNO_2$	Fe	0.1–1%
	Borax	Fe	1%
Glycol/water	Borax + Mercaptoben-zothiazole	All	1% + 0.1%
Acids, HCl	Ethylaniline	Fe	0.5%
	Mercaptobenzothiazole	Fe	1%
	Pyridine + phenylhydrazine	Fe	0.5% + 0.5%
	Rosin amine + ethylene oxide	Fe	0.2%
H_2SO_4	Phenylacridine	Fe	0.5%
Conc. H_3PO_4	NaI	Fe	200 ppm
Most acids	Thiourea	Fe	1%
	Sulfonated castor oil	Fe	0.5–1%
	As_2O_3	Fe	0.5%
	Na_3AsO_4	Fe	0.5%

Table 5.4 *(continued)*

System	Inhibitor	Metals protected	Concentration
Vapor condensate	Morpholine	Fe	Variable
	Ammonia	Fe	Variable
	Ethylenediamine	Fe	Variable
	Cyclohexylamine	Fe	Variable
Enclosed atmosphere	Cyclohexylamine carbonate	Fe	1 lb per 500 cu ft
	Dicyclohexylamine nitrite	Fe	1 lb per 500 sq ft
	Amylamine benzoate	Fe	Variable
	Diisopropylamine nitrite	Fe	Variable
	Methylcyclohexylamine carbonate	Fe	
Coating inhibitors	$ZnCrO_4$ (yellow)	Fe, Zn, Cu	Variable
	$CaCrO_4$ (white)	Fe, Zn, Cu	Variable
	Red lead	Fe	Variable

Cleaning may be accomplished with chemical cleaners, mechanical cleaners, ultrasonic energy, or thermal shock. Inhibitors can reach cleaned metal surfaces much more easily than they can reach heavily fouled or scaled surfaces.

5.8 Selection of Inhibitors

Many factors are involved in the selection of inhibitors, including the following:

- Identification of the problem to be solved
- Type(s) of corrosion present, see definitions and terminology
- Type of system (which influences the treatment method)
- Pressure
- Temperature
- Velocity
- Production composition
- System condition
- Efficiency of inhibitor
- Economy
- Compatibility with other chemicals and inhibitors. (The inhibitor must be able to treat in the presence of other materials such as phosphonates, polymers, bisulfites, and surface active agents, and must not interfere with their functions.)

5.8.1 Procedure for Selection

There are several approaches to be followed in selecting a proper inhibitor for a given system. An outside consultant or various suppliers can be asked for advice. Often, the particular combinations at

Table 5.5 *Corrosion inhibitor reference list*

Metal	Environmental	Inhibitor
Admiralty	Ammonia, 5%	0.5% hydrofluoric acid
Admiralty	Sodium hydroxide	0.6 mol H_2S per mol NaOH
Aluminum	Acid hydrochloric, 1N	0.003 M α-phenylacridine, β-naphthoquinone, acridine, thiourea,or 2-phenylquinoline
Aluminum	Acid nitric, 2.5%	0.05% hexamethylene tetramine
Aluminum	Acid nitric, 10%	0.1% hexamethylene tetramine
Aluminum	Acid nitric, 10%	0.1% alkali chromate
Aluminum	Acid nitric, 20%	0.5 hexamethylene tetramine
Aluminum	Acid phosphoric	Alkali chromates
Aluminum	Acid phosphoric, 20%	0.5% sodium chromate
Aluminum	Acid phosphoric, 20–80%	1.0% sodium chromate
Aluminum	Acid sulfuric, conc.	5.0% sodium chromate
Aluminum	Alcohol anti-freeze	Sodium nitrate and sodium molybdate
Aluminum	Bromine water	Sodium silicate
Aluminum	Bromoform	Amines
Aluminum	Carbon tetrachloride	0.05% formamide
Aluminum	Chlorinated aromatics	0.1–2.0% nitrochlorobenzene
Aluminum	Chlorine water	sodium silicate
Aluminum	Calcium chloride, sat.	Alkali silicates
Aluminum	Ethanol, hot	Potassium dichromate
Aluminum	Ethanol, commercial	0.03% alkali carbonates, lactates, acetates, or borates
Aluminum	Ethylene glycol	Sodium tungstate or sodium molybdate
Aluminum	Ethylene glycol	Alkali borates and phosphates
Aluminum	Ethylene glycol	0.01–1.0% sodium nitrate
Aluminum	Hydrogen peroxide, alkaline	Sodium silicate
Aluminum	Hydrogen peroxide	Alkali metal nitrates
Aluminum	Hydrogen peroxide	Sodium metasilicates
Aluminum	Methyl alcohol	Sodium chlorate plus sodium nitrite
Aluminum	Methyl chloride	Water
Aluminum	Polyoxyalkene glycol fluids	2% Emery's dimer acid (dilinoleic acid), 1.25% $N(CHMe_2)_3$, 0.05–0.2% mercaptobenzothiazole
Aluminum	Seawater	0.75% *sec*-amyl stearate
Aluminum	Sodium carbonate, dilute	Sodium fluosilicate
Aluminum	Sodium hydroxide, 1%	Alkali silicates
Aluminum	Sodium hydroxide, 1%	3–4% potassium permanganate
Aluminum	Sodium hydroxide, 4%	18% glucose
Aluminum	Sodium hypochlorite contained in bleaches	Sodium silicate
Aluminum	Sodium acetate	Alkali silicates
Aluminum	Sodium chloride, 3.5%	1% sodium chromate
Aluminum	Sodium carbonate, 1%	0.2% sodium silicate
Aluminum	Sodium carbonate, 10%	0.05% sodium silicate
Aluminum	Sodium sulfide	Sulfur
Aluminum	Sodium sulfide	1% sodium metasilicate
Aluminum	50% sodium trichloracetate solution	0.5% sodium dichromate

Table 5.5 *(continued)*

Metal	Environmental	Inhibitor
Aluminum	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate
Aluminum	Triethanolamine	1% sodium metasilicate
Brass	Carbon tetrachloride, wet	0.01–0.1 aniline
Brass	Furfural	0.1% mercaptobenzothiazole
Brass	Polyoxyalkene glycol fluids	2.0% Emery's acid (dilinoleic acid), 1.25% $N(CHMe_2)_3$, 0.03–0.2% mercaptobenzothiazole
Steel	55/45 ethylene glycol/water	1% sodium fluorophosphate
Copper	Fatty acids as acetic	H_2SO_4, $(COOH)_2$, or H_2SiF_6
Copper	Hydrocarbons containing sulfur	*p*-Hydroxybenzophenone
Copper	Polyoxyalkene glycol fluids	2.0% Emery's acid (dilinoleic acid), 1.25% $N(CHMe_2)_3$, 0.05–0.2% mercaptobenzothiazole
Copper & brass	Acid sulfuric, dil.	Benzyl thiocyanate
Copper & brass	Ethylene glycol	Alkali borates & phosphates
Copper & brass	Polyhydrate alcohol anti-freeze	0.4–1.6% Na_3PO_4 + 0.3–0.6 sodium silicate + 0.2–0.6% sodium mercatrobenzothiazole
Copper & brass	Rapeseed soil	Succinic acid
Copper & brass	Sulfur in lienzene solution	0.2% 9,10-anthraquinone
Copper & brass	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate
Copper & brass	Water/alcohol	0.25% benzoic acid or 0.25% sodium benzoate at a pH of 7.5–10
Galvanized iron	Distilled water	15 ppm mixture of calcium and zinc metaphosphates
Galvanized iron	55/45 ethylene glycol/water	0.025% trisodium phosphate
Iron	Nitroarylamines	Dibenzylaniline
Lead	Carbon tetrachloride, wet	0.001–0.1% aniline
Magnesium	Alcohol	Alkaline metal sulfides
Magnesium	Alcohol, methyl	1% oleic or stearic acid neutralized with ammonia
Magnesium	Alcohols, polyhydric	soluble fluorides at pH 8–10
Magnesium	Glycerine	Alkaline metal sulfides
Magnesium	Glycol	Alkaline metal sulfides
Magnesium	Trichlorethylene	0.05% formamide
Magnesium	Water	
Monel	Carbon tetrachloride, wet	0.001–0.1% aniline
Monel	Sodium chloride, 0.1%	0.1% sodium nitrate
Monel	Tap water	0.1% sodium nitrate
Nickel & silver	Sodium hypochlorite contained in bleaches	Sodium silicate
Stainless steel	Sulfuric acid, 2.5%	5–20 ppm $CaSO_4.5H_2O$
Stainless steel	Cyanamide	50–500 ppm, ammonium phosphate
Stainless steel 18-8	Potassium permanganate, conc., contained in bleaches	Sodium silicate
Stainless steel 18-8	Sodium chloride 0.4%	0.85% sodium hydroxide

(*continued overleaf*)

Table 5.5 *(continued)*

Metal	Environmental	Inhibitor
Steel	Citric acid	Cadmium salts
Steel	Sulfuric acid, dil.	Aromatic amines
Steel	Sulfuric acid, 60–70%	Arsenic
Steel	Sulfuric acid, 80%	2% boron trifluoride
Steel	Aluminum chloride–hydrocarbon complexes formed during isomerization	0.2–2.0% iodine, hydriodic acid, or hydrocarbon iodide
Steel	Ammoniacal ammonium nitrate	0.2% thiourea
Steel	Ammonium nitrate/urea solutions	0.05–0.10% ammonia, 0.1% ammonium thiocyanate
Steel	Brine containing oxygen	0.001–3.0% methyl-, ethyl-, or propyl-substituted dithiocarbamates
Steel	Carbon tetrachloride, wet	0.001–0.1% aniline
Steel	Caustic/cresylate solution from regeneration of refinery caustic wash solution, 240–260 °F	0.1–1.0% trisodium phosphate
Steel	Ethyl alcohol, aqueous or pure	0.03% ethylamine or diethylamine
Steel	55/45 ethylene glycol/water	0.025% trisodium phosphate
Steel	Ethylene glycol	Alkali borates & phosphates
Steel	Ethylene glycol	Guanidine or guanidine carbonate
Steel	Ethyl alcohol, 70%	0.15% ammonium carbonate + 1% ammonium hydroxide
Steel	Furfural	0.1% mercaptobenzothiazole
Steel	Halogenated dielectric fluids	0.05–4% ($\gamma - C_4H_3S)_4Sn$, $\gamma - (C_4H_3)_2Sn$, or $\gamma - (C_4H_3S)SnPH_3$
Steel	Halogenated organic insulation Materials as chlorinated diphenyl	0.1–2.4% $(NH_3)_2C_6H_3NHPh$, $o - MeH_4NH_2$, or $p - NO_2C_6H_4NH_2$
Steel	Herbicides such as 2,4-dinitro-6-alkyl phenols in aromatic oils	1.0–1.5% furfural
Steel	Isopropanol 30%	0.03% sodium nitrate + 0.015% oleic acid
Steel	1:4 methanol/water	To 4 L water and 1 L methanol add 1g pyridine and 0.05 g pyragallol
Steel	Nitrogen fertilizer solutions	0.1% ammonium thiocyanate
Steel	Phosphoric acid	0.01–0.5% dodecylamine or 2-amino bicyclohexyl and 0.001% potassium iodide, potassium iodate, or iodacetic acid
Steel	Polyoxyalkene glycol fluids	2.0% Emery's acid (dilinoleic acid), 1.25% $N(CHMe_2)_3$, 0.05–0.2% mercaptobenzothiazole
Steel	Sodium chloride, 0.05%	0.2% sodium nitrite
Steel	50% sodium trichloracetate solution	0.5% sodium dichromate
Steel	Sulfide-containing brine	Formaldehyde

Table 5.5 *(continued)*

Metal	Environmental	Inhibitor
Steel	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate
Steel	Water	Benzoic acid
Steel	Water for flooding operations	Rosin amine
Steel	Water-saturated hydrocarbons	Sodium nitric
Steel	Water, distilled	Aerosol
Tin	Carbon tetrachloride, wet	0.001–0.1% aniline
Tin	Chlorinated aromatics	0.1–2.0% nitrochlorobenzene
Tinned copper	Sodium hypochlorite contained in bleaches	Sodium silicate
Tin plate	Alkali cleaning agents, such as trisodium phosphate, sodium carbonate, etc.	Diethylene diaminocobaltic nitrate
Tin plate	Alkaline soap	0.1% sodium nitrite
Tin plate	Carbon tetrachloride	2% mesityl oxide, 0.001% diphenylamine
Tin plate	Sodium chloride, 0.05%	0.2% sodium nitrite
Titanium	Hydrochloric acid	Oxidizing agents, such as chromic acid or copper sulfate
Titanium	Sulfuric acid	Oxidizing agents or inorganic sulfates
Zinc	Distilled water	15 ppm mixture of calcium and zinc metaphosphates

Source: Maxey Brooke, Corrosion Inhibitor Checklist, Chem. Eng., 230–234 (December, 1954).

hand cannot be found in the literature. Hence, in addition to experience in the area, testing must be conducted to determine which inhibitor and in what concentration to use. Standard tests can be found in American Society for Testing and Materials (ASTM) publications and in the NACE Standard Test Methods.

A frequent cause of ineffective inhibition is loss of the inhibitor before it has a chance to contact the metal surfaces or effect the desired changes in the environment. An inhibitor might be lost by precipitation, adsorption, reaction with a component of the system, or by being insufficiently soluble or too slow to dissolve.

Typical examples of losses of an inhibitor due to these factors are precipitation of phosphates by the calcium ion, reaction of chromates with sulfides or organics, adsorption of inhibitors on suspended solids, and injection of a poorly soluble inhibitor without an adequate dispersing agent.

To avoid these problems, inhibitors should be tested in the actual fluids to be treated rather than in simulated environments. If possible, testing should be done in the process stream or in a small side stream.

5.8.1.1 Experience in the Area

It is always advantageous to check with other operators in the area to determine what chemicals and treatment methods are being used, and the results being achieved from these treatments. This information can be extremely valuable in providing a starting point for an inhibition program.

5.8.1.2 Inhibitor Evaluation Tests

The nominated inhibitor(s) should be evaluated (tested) with regard to function before selection for a system. Test(s) should include laboratory test(s) as well as field or operational tests.

5.8.1.3 Laboratory Evaluation Tests for Non-Aqueous Systems (Two-Phase Systems)

The laboratory test(s) should include one or more of the following test method(s), as required by the system to be treated:

- In the static test, the weight loss of a mild steel coupon after exposure to an inhibited solution is compared to the results obtained with an uninhibited solution under the same conditions.
- The wheel test is a dynamic weight-loss test, wherein a weighed coupon is immersed in the test fluid and rotated on a wheel at fixed rpm and temperature for a set period of time. This coupon is the "blank" or "control." In a system using an identical technique, a known concentration of the inhibitor is used. This test is run simultaneously with the control. At the end of the test period, the amount of weight loss suppression afforded by the inhibitor is determined. The wheel test is a widely accepted laboratory test for two-phase systems such as crude oil. This test is very useful, but not always reliable because of the restricted volume of the solvents and the difficulty in duplicating velocity and stagnation effects in real systems. The test procedure is described in NACE Report 10182.
- A recirculating dynamic test method can be used when it is desired to simulate field flow or operational conditions. Some of the parameters that should be controlled are the velocity of the corrosive medium, the oil:water ratio (in case of oil-field inhibitors), temperature, and dissolved gas and/or air concentration. Variables that can be imposed are the type of corrosive medium, the concentration of inhibitor, the effect of precorrosion of the test specimen, and the type of inhibitor treatment. This type of flow test provides a more severe test of inhibitor film life than the static bottle test. It furnishes a useful technique for the study of variables affecting inhibitor performance. Correlation between laboratory tests and field use of inhibitors is better using this technique than it is using data from the static test.
- The test for foaming is to obtain a sample of the fluid and gas from the process step, add the inhibitor in question, adjust the temperature to that corresponding to the process step and shake vigorously. If this test produces a stable foam, a potential problem exists. Pressure suppresses foam; some foams that exist at atmospheric pressure will not exist at system pressure.
- The test for emulsion formation is the same as for foams; the solution for the formation of an emulsion is to add a de-emulsifier, use another inhibitor or inhibit during shut-down. Most inhibitors will not cause emulsion formation at concentrations up to 250 ppm. Above this, be careful. The best preventative measure for the loosening of scale is to clean the system thoroughly, if possible, before the inhibitor is applied. An alternate or supplementary method in systems that are very sensitive to suspended solids is to protect the sensitive parts with temporary filters.

Similar laboratory evaluation tests should be performed for other systems.

The standard test methods should be in accordance with appropriate test methods in ASTM and NACE Standards such as NACE Standard TM-01-69 (1976 Revision). Scaling inhibitors and biological inhibitors should be tested in accordance with NACE Standard TM-03-74 and API-RP-38 accordingly.

5.8.1.4 Operational or field tests

After initial selection of the inhibitor(s) by means of laboratory tests, operational or field tests should be conducted before final selection. Tests should be conducted in the field or plant by monitoring the corrosivity of the fluid of interest in the presence of the inhibitor(s) initially selected. This is normally accomplished by treating the medium and measuring the effectiveness of the inhibitor with the appropriate standard methods. The initially selected inhibitor(s) should pass an operational or field test of 90 days minimum duration.

5.8.1.5 Concentration and performance of inhibitor (inhibitor efficiency)

Corrosion inhibitors are sold in solid or liquid form. Most solids are relatively pure, but sometimes a solid inhibitor is fused with another ingredient or encapsulated where a controlled rate of solubility is required. Liquids are usually preferred because of the ease with which they can be transported, measured, and dispersed.

Liquid inhibitors are rarely pure, for several reasons. Organic inhibitors seldom have optimum characteristics of viscosity, or freezing or boiling points; therefore, they are dissolved in an appropriate solvent to achieve the properties desired. Furthermore, it is often desirable to blend the inhibitor with a de-emulsifier, dispersant, surfactant, anti-foaming agent, or synergistic agent.

Liquid inhibitors are sold by the gallon, part of which is solvent. The amount of inhibitor present is expressed as percentage active, i.e. a gallon of inhibitor that is 20% active contains 20% by weight of inhibitor. In cold climates where inhibitors are likely to be stored or used in subfreezing temperatures, it may be impossible to use as concentrated a solution as in warmer climates without resorting to more expensive solvents.

Corrosion inhibitors are usually compared on the basis of their inhibitor efficiency, which is the percentage by which corrosion is lowered in their presence as compared with their absence. The inhibitor efficiency is calculated from the formula:

$$E = \frac{R_o - R_i}{R_o} \times 100 \tag{5.2}$$

where:

E = is inhibitor efficiency
R_o = is corrosion rate in the absence of inhibitor
R_i = is corrosion rate in the presence of inhibitor.

Example

Mild steel corroded in a cooling water at a rate of 1650 µm/yr (65 mpy). When 10 ppm of an inhibitor was added, the corrosion rate dropped to 380 µm/yr (15 mpy). What is the inhibitor efficiency?

Answer:

$$R_o = 1650 \text{ and } R_i = 380$$

Substituting in Equation (5.2),

$$E = \frac{1650 - 380}{1650} \times 100 = 77\%$$

Inhibitor concentrations are expressed as parts per million (ppm); for solids the units are on a weight basis, e.g., kilograms (or pounds) of inhibitor per million kilograms (or pounds) of fluid; and for liquid inhibitors, volumes are used, e.g. liters of inhibitor per million liters of fluid. To obtain the amount of inhibitor required for a given system, simply divide the amount of fluid to be inhibited by 1 000 000 and multiply by the ppm desired:

$$Q = \frac{V}{1\,000\,000} \times \text{ppm} \tag{5.3}$$

where:

Q = is the quantity of inhibitor required
V = is the amount of fluid to be inhibited
ppm = is the inhibitor concentration in parts per million.

Note that the quantity of inhibitor must be in the same units as those for the amount of fluid. ■

Example

What is the dosage of sodium chromate (a solid) required to add 10 ppm to 620 000 liters (165 000 gallons) of water?

Answer:

The volume of water is first converted to weight.

$$\text{kilograms of water} = 620\,000 \text{ liters} \times 1 \text{ lb} = (165\,000 \text{ gallons} \times 8.316/\text{gal})$$

Then:

$$V = 620\,000 \text{ kg } (1\,369\,500 \text{ lb})$$

$$\text{ppm} = 10$$

Substituting in Equation (3.3):

$$Q = \frac{620\,000}{1\,000\,000} \times 10 = 6.2 \text{ kg}$$

$$\left(\text{or } Q = \frac{1\,369\,500}{1\,000\,000} \times 10 = 13.7 \text{ lb}\right)$$

■

In conclusion, the inhibitor must meet certain requirements for each specific application, such as stability against temperature, time, and exposure to the corrosive environment. It must function at low concentrations and be easy to apply. Solubility characteristics must be designed for each application, and the inhibitor must be pumpable at the system temperature. It must be compatible with other chemicals in use, and must meet performance specifications. It must also be compatible with the system in which it is used, and not cause system upsets. It cannot be too toxic, and the flash point must be within specifications. Raw materials must be readily available and not too expensive, and manufacturing processes capable of control and reproducibility.

5.9 Economics of Inhibition

Prevention of corrosion by inhibition may be desirable for several reasons:

- To extend the life of equipment
- To prevent shutdowns
- To prevent accidents resulting from brittle (or catastrophic) failures
- To avoid product contamination
- To prevent loss of heat transfer
- To preserve an attractive appearance.

Potential savings for each of those goals must be evaluated to determine if a program of corrosion inhibition will be economical. Because costs are sometimes difficult to estimate, the best method is to obtain data on maintenance, replacement, etc., from past history of the system to be protected or from a similar system. Literature on the economics of inhibition is a tremendous aid in estimating costs.

There are several costs associated with the use of inhibitors. In fact, the cost of one or more of the following must be factored into any economic evaluation of corrosion inhibition:

- Installation of injection equipment
- Maintenance of injection equipment

- Purchase of inhibitor chemical(s)
- Monitoring inhibitor concentration(s)
- System changes to accommodate the inhibitor
- Operational changes to accommodate the inhibitor
- System cleaning
- Waste disposal
- Personnel safety equipment.

Economics of inhibitor use is an important requirement, but in cases where major shutdowns can be avoided through the use of inhibitors, the economic advantages of inhibition undoubtedly will be clear. Other cases will require detailed economic evaluations, which should be made through the use of formulas given in NACE Standard RP-02-72, 1972.

5.10 Environmental Factors for Corrosion Inhibitor Applications

5.10.1 Aqueous Systems

As mentioned earlier, there is no universal inhibitor for water systems, an inhibitor that may be satisfactory for one system may be ineffective or even harmful in another. The main factors that must be considered in the application of corrosion inhibitors to aqueous systems are salt concentration, pH, dissolved oxygen concentration, and the concentrations of interfering species.

This review of the use and properties of corrosion inhibitors in aqueous solutions illustrates some common inhibitor environment interactions. A process should be analyzed carefully and some tests made before a large-scale program of corrosion inhibition is initiated. When working with natural water, special attention must be given to its composition, particularly in regard to possibilities of natural inhibition and the presence of interfering ions.

5.10.2 Effects of Various Dissolved Species

Demineralized water is relatively non-corrosive toward steel because of its high electrical resistance (ohmic control) and low hydrogen ion concentration. However, when demineralized water is in contact with the atmosphere, it will absorb carbon dioxide and form carbonic acid, which will decrease its resistance so that significant corrosion of steel will occur, the cathodic reaction being primarily reduction of dissolved oxygen rather than reduction of hydrogen ions.

In this case, minimal concentrations of inhibitors such as sodium chromate, sodium nitrite, polyphosphates, sodium benzoate, or borax are effective. Steel is easily passivated in demineralized or distilled water because the pH is neutral and there are no dissolved ions to interfere with formation of the passive layer.

Industrial and domestic waters contain dissolved substances that affect their aggressiveness and corrosion inhibitor requirements in various ways, depending on the nature of the substances. The most common dissolved substances and their effects on corrosion inhibition are as follows.

5.10.2.1 Oxygen (O_2)

In neutral water, oxygen causes corrosion; therefore, if it is reduced to less than 0.1 ppm by scavenging compounds or by stripping, sufficient control is provided for some systems, e.g. in boilers and hot water supplies. Oxygen can be utilized in passivating steel by adding a passivating inhibitor. Organic inhibitors are seldom effective against oxygen attack unless they contain passivating groups such as benzoate or nitrite.

5.10.2.2 *Chloride* (Cl^-)

Steel, like many other metals, is more difficult to passivate in the presence of the chloride ion, therefore, a higher concentration of passivating inhibitor is required. Non-passivating inhibitors must also be used in higher concentrations because chloride ions are strongly absorbed by steel.

5.10.2.3 *Sulfate* (SO_4^{2-})

The effects of sulfate on passivity are similar to those of chloride, but to a lesser degree. Sulfates or chlorides must not be allowed to build up in a system by evaporation because depassivation may occur.

5.10.2.4 *Bicarbonate* (HCO_3^-)

Bicarbonate in hard water can be utilized for natural inhibition by the formation of precipitates. In soft water, corrosion inhibitors must be used if excess carbon dioxide is present because of the acidic conditions it produces.

5.10.2.5 *Sulfides* (S^{2-})

Sulfides precipitate many metal ions, e.g. inhibitors containing zinc cannot be used. Oxidizing inhibitors are reduced by sulfide to form free sulfur. They are effective only if an excess above the amount required to react with sulfide is used and the collodial precipitate of free sulfur can be tolerated.

5.10.2.6 *Metal Cations*

Sodium (Na^+) and potassium (K^+) ions have no particular effects on inhibitors; calcium (Ca^{2+}) and magnesium (Mg^{2+}) may be used to form protective precipitates, but at high concentrations they interfere with inhibitors by precipitating non-protective deposits and also by precipitating inhibitors such as phosphate (PO_4^{3-}) and silicate (SiO_3^{2-}). Very small concentrations of heavy metal ions, such as copper and mercury, can cause severe interference with inhibitors.

5.10.2.7 *Acid* (H^+)

Hydrogen ions increase corrosion rates and increase the difficulty of passivating steel. Passivation is used in sulfuric (H_2SO_4) and phosphoric acids (H_3PO_4), but not in hydrochloric acid (HCl). Non-passivating organic or cathodic inhibitors (e.g., guanidine or sodium arsenate) are preferred in pickling acids to avoid the disastrous consequences of depassivation.

5.10.2.8 *Alkali* (OH^-)

In alkaline solutions, corrosion of steel is controlled by the rate of oxygen diffusion through the precipitated corrosion product (usually ferrous hydroxide, $Fe(OH)_2$), so corrosion rates are low. Steel is easily passivated in alkaline solutions. Amphoteric metals such as aluminum, zinc, and lead corrode slowly at low alkali concentrations, but above pH 9.0 their rates are very high and inhibitors are required.

5.10.2.9 *Water of Low-to-Moderate Salt Concentrations*

Water of low-to-moderate salt concentrations is encountered in municipal water systems, cooling waters, marine and offshore activities, and oil-field water injection systems. Because metals adsorb ions of dissolved salts in water, an inhibitor has more difficulty in reaching the metal surface and

displacing adsorbed ions than it has in dimineralized water; hence, a higher concentration of inhibitor is required.

Furthermore, chloride ions have a depassivating effect, i.e. they make it more difficult to control corrosion by passivating inhibitors. Thus, it is important to maintain inhibitor concentrations at a safe level in waters containing dissolved salts, particularly the chlorides.

Municipal drinking water cannot be treated with most inhibitors because of their toxicity. Fortunately, treatment with lime to raise the pH usually affords sufficient protection to steel or cast iron water pipes.

If the water is high in chlorides or sulfates, then polyphosphates are used for added inhibition. Silicates also may be used in municipal waters, but they have the disadvantage of forming precipitates with iron and calcium that scale pipes and heat transfer surfaces.

Cooling water systems may be either recirculating or once-through types. In closed recirculating systems, oxygen can be excluded, and corrosion often can be controlled by adjusting the pH to an alkaline value.

Recirculating systems are more easily controlled by inhibitors since higher concentrations can be applied because the water is reused. Sodium chromate or sodium nitrite are both effective in all-steel, closed recirculating systems.

Sodium nitrite may be formed from ammonia by reduction at cathodic sites; therefore, it should not be used in systems that include brass or copper, since these materials are subject to stress corrosion cracking by ammonia.

Glycol–water mixtures, such as those used to cool engines and to transfer solar heat, cannot be inhibited with oxidizing inhibitors such as chromate or nitrite because the glycol is oxidized. This not only consumes the inhibitor, but also forms organic acids that attack the cooling system. Such cooling systems are usually inhibited with a mixture of borax (for maintaining an alkaline pH) and mercaptobenzothiazole, which inhibits the corrosion of brass and copper. Borax alone is satisfactory for steel in contact with glycol–water mixtures, but borax and glycol attack zinc galvanizing rapidly, and attack the zinc in brass due to the formation of complex zinc compounds at low temperatures. Thus, the addition of mercaptobenzothiazole is necessary in mixed-metal cooling systems.

A soluble oil also is often added to increase protection and to lubricate moving parts in cooling systems. In some mixed-metal systems, silicates and nitrates are now used. Amine phosphates have also long been used in such systems.

Once-through cooling systems require inexpensive corrosion inhibitors. In open systems, corrosion is more severe and good inhibition is imperative. The situation is similar to that in municipal water supplies, so comparable remedial measures, namely addition of lime or polyphosphates, are used. In waters that are very corrosive due to high chloride concentrations, chromates or nitrites may be required in addition to polyphosphates.

Waters that may contain appreciable quantities of organic matter, such as seawater and oil-field injection brines, are usually not inhibited with oxidizing inhibitors such as chromate and nitrite because of the high consumption of inhibitor through oxidation of the organics.

Non-oxidizing inorganic inhibitors such as sodium silicate must also be used in high concentrations due to the high chloride content of brines. Generally, organic inhibitors offer the best means for protection in organic-contaminated brines. Concentrations of only 10 to 20 ppm of inhibitors such as the fatty amines often effectively control corrosion in oil-field brines.

5.10.2.10 High Salt Concentrations

Extremely high salt concentrations are used in aqueous solutions for heat transfer in refrigeration systems. The temperatures encountered are always low, and since the brines are recirculated, a high concentration of inhibitor can be maintained economically.

Sodium chromate is effective in refrigeration brines, provided there is no limitation due to its toxicity. If physiological effects are a factor, then disodium phosphate can be used, although it is not as effective as sodium chromate in controlling corrosion.

5.10.2.11 Effects of pH

The pH of aqueous solutions is extremely important in determining the type of corrosion inhibitor that is most effective and most economical. Natural hard waters retain calcium compounds, including calcium carbonate ($CaCO_3$) and calcium bicarbonate ($Ca(HCO_3)_2$), along with carbon dioxide, in solution. There is an equilibrium among these species, as shown by Equation (5.4).

$$\underset{\text{insoluble}}{CaCO_3} + CO_2 + H_2O \leftrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2} \tag{5.4}$$

At high temperatures the reverse reaction occurs, and heated surfaces become coated with $CaCO_3$. A protective scale is also produced when $Ca(HCO_3)_2$ becomes alkaline in the region of a cathodic area. The scale thus deposited inhibits corrosion by reducing the cathodic area, restricting diffusion of cathodic depolarizers, and increasing ohmic resistance.

This scale is often developed on cathodically protected steel surfaces in seawater, and is often called a calcareous deposit. For this reason, some natural hard waters are less corrosive than softened waters. The addition of zinc sulfate ($ZnSO_4$) in alkaline solutions also inhibits corrosion by precipitating insoluble zinc hydroxide ($Zn(OH)_2$) on the cathodic area.

Hydrogen sulfide is a particularly troublesome problem. The dissolved gas attacks steel only slowly when first exposed, due to the formation of a protective layer of iron sulfide. The iron sulfide film affords only temporary protection, however, because it becomes permeable to hydrogen sulfide, and the corrosion rate increases with time, producing blistering, high metal loss, and possibly hydrogen embrittlement.

Organic corrosion inhibitors prolong the interval preceding higher corrosion rates, but the iron sulfide film eventually prevents access of the inhibitor to the steel surface and, as a result, the corrosion process can proceed uninhibited.

The most effective chemical control measures against hydrogen sulfide (sour) corrosion are removal of the hydrogen sulfide from the water by counter-current gas stripping or by cleaning the steel periodically with acid to allow access of the inhibitor to the metal surface. Steel sometimes can be cleaned sufficiently for inhibition to be effectively by the use of a powerful wetting agent.

5.10.2.12 Strong Acids

High acid concentrations are encountered in pickling processes, oil-well acidizing, and during the transportation of acids for use in chemical processes. Hydrochloric acid of all concentrations requires an inhibitor if steel is to be used. The use of an inhibitor in pickling processes also allows the acid to dissolve scale from steel without appreciable attack on the metal.

Pickling acids are effectively inhibited by adding about 0.2% of organic compounds such as anilines, pyridines, thiourea, or sulfonated castor oil. Cathodic inhibitors such as arsenates (As_2O_3), e.g., sodium arsenate (Na_3AsO_4), are also good inhibitors for pickling acids, but are less popular than organics because they cause blistering and hydrogen embrittlement of some steels. Arsenic compounds should never be used in fluids that are to be catalytically processed because arsenic is a poison to most catalysts.

Sulfuric and phosphoric acid concentrations up to 70% can be inhibited by methods similar to those used for hydrochloric acid. Concentrations of sulfuric acid higher than 70% are strongly oxidizing, attack steel slowly, and do not require inhibition. Fertilizer-grade phosphoric acid (73% black acid) attacks steel readily and usually is inhibited with potassium iodide. Organic inhibitors are not effective

in concentrated phosphoric acid when used alone, but it has been reported that a lower concentration of potassium iodide is required for inhibition if a fatty amine is also added.

5.10.2.13 Non-Aqueous Systems

As mentioned earlier, corrosion in non-aqueous liquids such as fuels, lubricants, and edible oils is usually caused by the small amounts of water often present. Water is slightly soluble in petroleum products, and its solubility increases with temperature. If a non-aqueous solvent is saturated with water and the temperature is lowered, then some of the water will separate to attack steel that it contacts.

Inhibition of corrosion of aluminum when in contact with halogenated solvents is more difficult. Aluminum in contact with many of the one- and two-carbon chlorocarbons can explode after a varying incubation period if the solvent is dry. A few parts per million of water will inhibit the reaction. On the other hand, if water is added exceeding the limited solubility in the solvent, the water layer will become highly acidic from hydrolysis of the organic compound. Thus, inhibition in systems containing these materials must be approached with caution.

Water also inhibits the stress corrosion cracking of steel in ammonia, and titanium in methanol, as well as attack on titanium by "dry" chlorine. A trace of water (0.001%) in liquid hydrogen fluoride (HF) behaves as a passivating inhibitor for nickel. This is an extreme example of the importance of solvent–inhibitor interactions. The exact mechanism of inhibition by water in HF is unknown, but the passivating effect is similar to that observed on steel in the presence of chromates in aqueous solution.

Solubility is an important factor to be considered in evaluating corrosion inhibitors for non-aqueous fluids, because they do not have the tremendous solvating power of water. Because an inhibitor must be transported through the environment to sites where corrosion occurs, it must be either soluble in the environment or sufficiently dispersed in fine droplets that settling does not occur. Also, the inhibitor must not form filter-plugging insoluble products by reaction with metals or components of the non-aqueous fluid. Some corrosion inhibitors formerly used in gasoline were found to react with zinc in galvanized fuel tanks to form a precipitate that clogged fuel filters.

Testing inhibitors in non-aqueous media is more difficult than in aqueous solutions, especially if corrosion is due to water separating to form a two-phase system. This condition is difficult to duplicate in the laboratory, and polarization curves cannot be used effectively because most non-aqueous solvents are non-conductors. Furthermore, corrosion coupons placed in pipes or tanks carrying fuel or similar products may give misleading results because they may not be contacted or wetted by the water phase.

A widely accepted laboratory test for two-phase systems (called the wheel test) consists of alternately wetting a corrosion specimen by the organic and water phases by rotating a bottle containing the two phases. This test is very useful, but not always reliable because of the restricted volume of the solvents and the difficulty in duplicating velocity and stagnation effects in real systems.

5.10.3 Gaseous Environments

As mentioned earlier, gaseous environments include the open atmosphere, the vapor phase in tanks, natural gas in wells, and the empty space in packaging containers. Here again, water and oxygen are the principal corrosive agents, but the main problem in providing inhibition is to transport the inhibitor from a source to the sites where corrosion may occur.

5.10.3.1 The Open Atmosphere

Inhibitors of corrosion in the open atmosphere are applied directly to the metal surfaces to be protected. The most common method is the use of chromates in paints. Zinc chromate and red lead

are used in primer coats. Rivet heads are coated with a slurry of micro-encapsulated zinc chromate. When the rivet is driven against another surface, the capsules rupture to provide lasting inhibition to the crevice under the rivet head. Volatile inhibitors are never used in the open atmosphere because they are impractical and cannot saturate the vapor space.

5.10.3.2 Closed Vapor Spaces

The walls of tanks above a water line are subject to extensive corrosion because the relative humidity is always high and oxygen is plentiful if the tank is vented to the atmosphere.

Where water contamination is not a factor, a layer of oil on the surface helps to maintain a low humidity and, as the level is raised and lowered, the walls are coated with a layer of oil. The oil may contain an organic inhibitor and an agent (usually an amine) to cause the oil to spread on the metal surface. An oil layer containing about 15% lanolin has been used in ship ballast tanks to control corrosion.

Gas wells corrode mostly in the reflux zone, which is an area of the well somewhere between the bottom and the wellhead, where condensation occurs. As the gas flows up the well, its temperature drops due to expansion, and this causes condensation when the temperature reaches the dew point of the gas. Volatile inhibitors such as formaldehyde and ammonia, injected into gas wells have been used successfully to inhibit corrosion. Many gas wells today are protected by injecting amine inhibitors continuously, in batches, or by squeezing, which means they coat the well when injected and also enter the gas stream partially by vaporization and partially by entrainment.

Packaged materials may be protected from corrosion in several ways. Packages that can be sealed and that contain parts that cannot be coated with an inhibitor or exposed to volatile inhibitors (such as electronic parts) are protected by placing a desiccant, such as silica gel, in the package to maintain the humidity at a low level.

Vapor phase inhibitors (VPIs) can be placed in a package in bulk or by wrapping an article in paper impregnated with a VPI. These compounds are volatile organics, so the package in which they are used must be fairly well sealed. The most common VPIs in use are dicyclohexylamine nitrite (DHN) and cyclohexylamine carbonate (CHC). These inhibitors are very effective for steel, but they should be tested if metals other than steel are present because they attack some non-ferrous metals.

Inhibited coatings provide a cheap, effective method for controlling corrosion of packaged materials. Easily strippable coatings that do not harden are called soft coatings or slushing compounds. Oils and greases containing amines may be used. Steel and zinc articles can be protected with a thickened aqueous solution of sodium benzoate or sodium nitrite.

Metals that are very sensitive to hydrogen sulfide, such as copper and silver, are protected by enclosing them in paper impregnated with copper or zinc compounds. These materials are not corrosion inhibitors in a strict sense since they adsorb gaseous sulfur compounds to prevent reaction with the silver or copper.

5.10.3.3 Effect of Elevated Temperatures

As mentioned earlier, most effects of elevated temperatures are detrimental to corrosion inhibition. High temperatures increase corrosion rates (about double for a 15 °C rise at room temperature), and they decrease the tendency of inhibitors to adsorb on metal surfaces. Precipitate-forming inhibitors are less effective at elevated temperatures because of the greater solubility of the protective deposit.

Thermal stability of corrosion inhibitors is an important consideration at high temperatures. Polyphosphates, for example, are hydrolyzed by hot water to form orthophosphates, which have little inhibitive value. Most organic compounds are unstable above about 200 °C (400 °F), hence they may provide only temporary inhibition at best.

In neutral or slightly alkaline, oxygen-free aqueous systems, corrosion of fairly clean steel occurs at a very low rate at elevated temperatures. This principle is the basis for most boiler water treatment to prevent corrosion, i.e., treatment is designed to provide alkalinity, to remove oxygen, and to prevent scale deposition. Other additives are also used to prevent foaming, but these will not be considered here.

In oxygen-free hot water, steel is protected by formation of a natural coating of magnetite (Fe_3O_4 or black rust) formed by the reaction:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{3.5}$$

If oxygen is present, then non-protective Fe_2O_3 (red rust) is formed. At elevated temperatures, oxygen is removed readily from boiler waters by reaction with sodium sulfite or hydrazine. Hydrazine is preferred because it does not increase the salt content of the boiler water; moreover, it reacts faster than sodium sulfate at elevated temperatures, the dosage required to react with a given amount of oxygen is lower, and it is easier to apply because it is a liquid.

Boiler waters are maintained at an alkaline pH to facilitate formation and maintenance of the Fe_3O_4 protective film. It is desirable to use an additive that will be carried into steam condensate lines to maintain an alkaline condition in these areas also. Volatile amines such as ammonia, morphine, cyclohexylamine, and octadecylamine are used.

Deposition of scales in boilers reduces heat transfer and produces pitting-type corrosion. Water softeners often are used to treat boiler feed to remove objectionable ions such as calcium, magnesium, but usually a scale inhibitor such as sodium phosphate also is added. The phosphates prevent scaling by increasing the supersaturation of $CaCO_3$ and $CaCO_4$ in water. In high-pressure, high-temperature boilers, demineralized water often is used. In these cases, only oxygen removal with hydrazine is required.

High temperatures always increase the rate of attack of metals in acids because the driving force for the anodic and cathodic reactions is greater and hydrogen overvoltage is decreased. Other factors such as the greater solubility of corrosion products and the higher rate of solution of metal oxides also increase the rate of attack.

While hot acids are handled best by resistant alloys or coated steel, an exception is the acidizing of oil wells. It is impractical to coat or line oil-well casing because the coating is soon destroyed by the insertion of tools, etc. Bottom hole temperatures of oil wells are often 93 to 150 °C (200 to 300 °F) and sometimes as high as 230 °C (450 °F). Inhibitors for acids used to increase the permeability of oil-producing formations (usually HCl) are effective, but have temperature limitations. Amine-type pickling acid inhibitors are often used for oil-well acidizing.

6

Requirements for Corrosion Control in the Petroleum and Petrochemical Industries

The petroleum industry contains a wide variety of corrosive environments. Thus it is convenient to group all these environments together. Corrosion problems occur in the petroleum industries in at least four general areas, as follows:

- Exploration (drilling and completion of oil or gas wells)
- Production
- Transportation and storage
- Petroleum refineries and petrochemical plants.

6.1 Exploration

Corrosion is one of the problems that must be reckoned with in the successful drilling and completion of an oil or gas well. Recognition of the causes of corrosion in this environment, as in others, has led to the development of numerous corrosion control techniques.

It is well known that environmental components such as oxygen, carbon dioxide, hydrogen sulfide, and dissolved salts accelerate corrosion attack. These corrosion accelerators are commonly encountered in drilling and completion fluids and in many instances all are present.

To offset their corrosive effects several techniques are used, including dilution, concentration, precipitation, neutralization, and chemical inhibition. Living organisms are not usually classified as corrosion contaminants, but they have the ability to produce corrosives to the extent that they, too, are an important consideration in corrosion control.

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6.1.1 Factors Important in Corrosion Attack During Drilling and Their Control

6.1.1.1 Micro-Organisms

Micro-organisms are common to drilling and completion fluids and can produce hydrogen sulfide, carbon dioxide, or organic acids. Some bacterial species, including *Desulfovibrio desulfuricans*, also increase corrosion by metabolically depolarizing the cathode. Because of the prolific nature of bacteria in these environments, both biostats and biocides are often used for their control.

6.1.1.2 Mechanical and Metallurgical Factors

Corrosion due to mechanical and metallurgical problems also exist. Metal tools used in drilling wells are often softer than the formation being penetrated. The abrasiveness of formation solids can easily erode protective films from drilling equipment, leaving metal exposed to corrosion-erosion attack. Mechanical and chemical separation of abrasive solids helps control this attack. It is difficult, however, to control stress concentrations in a string of drill pipe that may reach many kilometers into the earth.

Stress increases corrosion attack and must be controlled through proper design and use of equipment, as well as by reduction of environmental corrosives. For example, corrosion pits concentrate stress and are prime initiation points for corrosion fatigue cracks, which are the major cause of drill pipe failure. It is easily understood that corrosion problems become more critical as well depth increases, because among other things, high temperature becomes one of the more critical problems faced in many deep drilling projects.

6.1.1.3 Effect of High Temperature

There are two generally accepted high-temperature corrosion effects in drilling and packer fluid environments. As temperature increases, corrosion attack increases exponentially, and high-temperature degradation products of chemical additives increase environmental corrosiveness.

Thermal stability is a primary prerequisite for materials involved in chemical corrosion control under high-temperature conditions. Dilution, precipitation, and corrosion inhibition are also used to combat this problem.

6.1.1.4 Time Factors

Time is always an important factor in corrosion control. The current trend in oil-well drilling that requires probing deeper strata of the earth increases equipment exposure time under the critical conditions.

Good practice involves decreasing the area of equipment surface exposed, the exposure time and the critical conditions. Drill pipe with and internal plastic coated and sealed bearing bits are two examples of decreased equipment surface exposure. Increasing penetration rates by optimizing drilling conditions has played an important role in reducing equipment exposure time.

Use of temperature-stable materials, corrosion inhibitors, or converting to non-corrosive oil systems also changes conditions. Not all practices can be considered beneficial, even though they improve one or more of the detrimental conditions. As an example, air or mist drilling greatly increases the penetration rate and therefore decreases equipment exposure time. Although this technique is often considered economical, corrosive conditions are almost always severe and require correction. The relationship between the chemical, mechanical, and time factors involved in controlling corrosion caused by drilling and packer fluids has been recognized for many years. Early recognition of corrosion problems in the drilling industry led to the development of some of the technology used in current exploration and production practices.

6.1.1.5 Problems Related to Packer Fluids

Drilling fluids are often left as packer fluids in the tubing and casing annuli. The "fill-in fluid" must function in a different way from the drilling fluid, because dynamic circulating drilling conditions are changed to a static fluid column. While drilling, the fluid must remove tremendous quantities of formation debris from the bore hole, some of which is trapped in the circulating fluid and may present a corrosion problem when the mud is left as a packer fluid.

One function of the packer fluid is to stabilize and maintain the entrained materials in suspension. This fluid must be of sufficient density to contain the well pressure in the event of a pipe failure. Under long-term, static conditions, detrimental changes may take place that cannot be rectified easily.

Packer fluids must be conditioned to function for years, because no opportunity is afforded for correction without great expense. Corrosive contaminants, such as carbon dioxide and hydrogen sulfide are produced by bacterial action, thermal degradation, or electrochemical reduction. The fluid placed in the annular space of the well requires careful selection for the assurance of successful and economical completion.

6.1.2 Some Problems Related to Water-Based Fluids and Their Control

Water-based drilling fluids present corrosion problems primarily because they are subject to contamination from corrosion accelerators such as oxygen, carbon dioxide, hydrogen sulphide, or salts that are always present in varying quantities. The sources and effects of these contaminants have been the subject of numerous investigations. Early investigators were primarily concerned with oxygen, which is still a major problem today.

For example, oxygen scavenger treatments are being adjusted through measurements with an oxygen meter and electrical corrosion probes. The quick response of these instruments is an important benefit in controlling corrosion during drilling. They permit measurements at pump suction and flow line. Oxygen scavenger treatments are adjusted to keep suction readings the same as or less than those of the flow line. This procedure is based on the fact that oxygen enters the pump suction and is consumed in reactions on the drill string, while circulating back through the hole to the flow line.

Experience has shown that a sulfite residual in the drilling fluid is necessary to take care of oxygen pickup during "trips," chemical or water additions, and mud-pit cleaning. The most effective control of oxygen corrosion is to keep oxygen out of the system. This is difficult, because the drilling fluid is exposed to the atmosphere as it circulates through the pits. However, carelessness is often the cause of excessive oxygen pickup. For example, the improper use of mud guns or mud hoppers is a common occurrence, and results in added oxygen contamination. Aerated muds, oxygen-contaminated make-up water, and oxidizing chemicals all are sources of this environmental corrosion accelerator. In the case of air or aerated drilling, corrosion is a most serious problem.

In aerated seawater, corrosion rates of more than 11.5 mm/yr (450 mpy) or (18 lb/sq-ft/yr) have been measured with down-hole coupons. In drilling fluids the control of corrosion rates below 1.27 mm/yr (50 mpy) or (2 lb/sq ft/yr) with uniform corrosion is considered a practical objective.

Attack from oxygen in this environment is almost always in the form of pitting, which in a short time can produce irreversible damage to drilling equipment. Sharp-bottomed pits are especially damaging to the drill pipe because they cause stress concentrations that increase susceptibility to fatigue failure. Pitting is one of the most deceiving forms of corrosion under drilling conditions. Severe pitting will not always result in the expected associated failures. Pits with round bottoms do not cause failures as often as those with sharp profiles. Longer exposure and higher stresses are required to produce failures when pits have wide-angled geometry. What makes a pit around or sharp bottomed is not clearly understood, but the grade of steel, environment, and stress conditions are all thought to be important factors.

Proper environment control has a strong influence on both the form and rate of corrosion attack. When pitting occurs, mitigation techniques should strive to lower the corrosion rate to less than 1.27 mm/yr (50 mpy) and make the attack uniform. A rate expressed in mm per year has little meaning unless corrosion is uniform, because pits concentrate stress and lead to premature fatigue failures of drilling equipment. In drilling fluid environments, pits, which often are the result of corrosion concentration cells, affect stress and fatigue life. Concentration cells are caused by a difference in the concentration of ions on the affected metal surfaces. Conditions for this to occur in drilling fluids are most often caused by incomplete barriers such as mud solids, scale, and corrosion by-product deposits on the exposed drilling equipment.

Since ion concentration underneath the barrier is different from that on clean metal, an active corrosion cell can exist. In oxygen-contaminated fluid, concentration cells are serious pitting accelerators. Elimination of the barrier or a difference in ion concentration is needed to control this cause of pitting.

Sand blasting has been used to clean drill pipe and remove barriers and scale from the metal. Control methods most often used on operating equipment include frequent treatments with oil-soluble, organic amine inhibitors applied directly to the affected metal surface. These must penetrate and cover either the anodic or the cathodic area (or both) of the corrosion cell in order to stifle the cell.

Thick scale or corrosion by-products that prevent the inhibitor from reaching the base metal interfere with protection. Mechanical removal of the barrier is necessary under these conditions. Controlling concentration cell corrosion by the removal of an offending ion, such as oxygen, would be impractical in aerated drilling systems. However, the reduction of oxygen is often achieved in normal drilling by the addition of tannates, quebracho, or lignosulfonates. Sodium sulfite is now being used in non-dispersed, low-solids polymer muds. These chemicals, along with organic amine treatments, can provide significant protection against oxygen corrosion (concentration cell).

6.1.2.1 How Amines are Used

There is some discussion underway on the merits of amine inhibitors for controlling oxygen corrosion. Experience shows that they are ineffective at low concentrations, but work better if applied directly to the affected metal as mixtures of 5 to 20% inhibitor in oil or water.

Oxygen corrosion in drilling is not limited to aerated systems, however make-up water contaminated with oxygen has a strong influence on corrosion of drilling equipment. In some drilling operations, over 16 m^3 (1000 barrels) of water per day are used. In one case, approximately 20% of the drill pipe wall was penetrated by pitting in three days' exposure. Approximately 22 000 liters of fresh water were added during this period.

Corrosion by-products from the pits were identified as oxides of iron, clearly pointing to oxygen as the major cause of corrosion and providing an indication of the damage that can result from simple make-up water additions. Polymer-type drilling fluids are susceptible to strong oxygen corrosion attack because they normally do not contain thinners and are generally of a low pH. These fluids tend to foam and entrap air. Oxygen scavengers, organic inhibitors and defoamers are commonly required in these systems.

Oxidizing chemicals, such as chromates, are often used in small quantities as a thinning agent in drilling fluids. An increase in corrosion (pitting) has frequently been experienced following chromate additions. Additions of both oxygen-contaminated water and oxidizing chemicals will continue because they are useful and necessary in drilling operations. This is an important point, because corrosion is only one of the factors involved in a complex mixture of mechanical and chemical considerations. The primary objective is to drill a well safely and economically, so consideration must be given to methods that permit this to be done most efficiently. If the use of materials that cause an undesirable increase in corrosion cannot be avoided, then adequate inhibitor treatments should be used to control corrosion.

6.1.3 Techniques to Control Corrosion in Drilling Operations

The acid-forming gases, carbon dioxide and hydrogen sulphide, are serious environmental corrosion accelerators that must be dealt with in drilling fluids. These are often associated with the hydrocarbons of the produced crude oil or gas, as well as the formation water and are a major cause of corrosion in the petroleum industry. They cause both general attack and stress corrosion and produce highly insoluble corrosion products that often are detected in pits and fatigue cracks in drilling equipment.

6.1.3.1 Influence of Gas Contamination

Contamination by carbon dioxide or hydrogen sulfide from the formation can be quite serious if large volumes of gas are allowed to enter the fluid column. This is best prevented by properly controlling the hydrostatic pressure. When drilling operations are at a pressure near that of the formation or otherwise under pressure, larger quantities of formation gas can enter the mud and more acid contamination will occur.

Contamination can occur while drilling either gas- or water-bearing formations, so it is customary to provide an alkaline buffer to help neutralize them. In most cases the alkaline buffer is used to preserve drilling fluid properties, as well as to reduce corrosion problems. Alkaline materials have limitations and may be insufficient to neutralize the acid gases if serious contamination is occurring. Under these conditions much of the gas may be vented to the atmosphere from the surface pits or disposed of even more efficiently by degassing equipment. In addition, drilling fluid properties can be adjusted to facilitate the escape of the gas.

Hydrogen sulfide in sufficient quantities is poisonous if uncontrolled and will be dangerous to rig crews. When control is necessary, metallic salts can be added to the fluid to precipitate the sulfides and reduce the danger. Compounds such as zinc oxide or zinc carbonate are used to combine with sulfide ions to form highly insoluble precipitates in strongly basic muds. This reaction reduces the harmful effects of the sulfide from a health standpoint and possibly aids in mitigating corrosion. However, the long-term effects of a continuous build-up of a zinc sulfide precipitate in the drilling fluid is unknown and may become a problem. For example, if the pH is lowered, hydrogen sulfide can be regenerated. While this reaction can be controlled in drilling fluids, the pH is naturally reduced under packer fluid conditions. Some caution should be exercised in the use of a packer fluid in which a semi-stable sulfide compound is present; when high-strength tubing and casings are used, a packer fluid free of sulfide precipitate is called for. Zinc oxide and carbonate compounds are only sparingly water soluble, but the solids still react with the sulfide ion. The insoluble character of the zinc materials allows for addition to the drilling fluid as a pre-treatment and buffer against sulfide contamination.

6.1.3.2 Copper as a Corrosion Hazard

Copper compounds also are used as sulfide ion precipitators. The copper compounds are efficient in precipitating sulfide, but can cause accelerated corrosion of steel. Basic copper carbonate is used to combat the sulfide ion problem. Copper carbonate has very limited solubility in water and, as with zinc compounds, the solids react with sulfide ions.

The limited solubility of copper carbonate in drilling fluids becomes a corrosion problem as a result of an electrochemical reaction, whereby the copper ion is displaced from solution by iron going into solution, causing metallic copper to be plated on the steel equipment. For this reason, copper compounds are not generally recommended in drilling fluids.

6.1.3.3 Influence of Temperature

Acid gas contamination has resulted from drilling fluid materials that have been altered by temperature, microbiological activity, or electrochemical effects. Contamination originating from thermal breakdown of drilling fluid additives is conditioned by time and temperature.

Serious breakdown into carbon dioxide or hydrogen sulfide of many commonly used organic materials containing carbonyl or sulfur-oxygen groups begins at approximately 150 °C (300 °F). Thermally stable materials should be used when well temperatures are expected to exceed the 150 °C (300 °F) range for extended periods because thermal degradation tends to destroy drilling fluid properties.

Water dilution or small additions of sodium chromate are often used together with other additives to preserve thermally degraded mud fluids. Both alternatives add oxygen and accelerate corrosion. During drilling operations, organic amine corrosion inhibitor treatments applied to the drill string and alkaline materials in the drilling fluid are usually effective in offsetting the corrosive effects of thermally degraded mud fluid. The addition of drilling fluid additives is a serious problem in packer fluids.

6.1.3.4 Biological Effects

Micro-organisms readily attack drilling fluid additives, resulting in their chemical breakdown into carbon dioxide, hydrogen sulphide, and other degradation products. The breakdown of these additives can result in significant detrimental changes for controlling fluid properties and corrosion.

Alkaline materials are considered biostats in drilling fluids, but for efficient micro-organism kill, biocides are used. The most readily measurable effect of micro-organisms in drilling fluid is their consumption of chemicals, which results in the loss of the desired filtration control and rheological properties. Bacterial cultures can be made from the drilling fluid to determine their presence and populations so that pH adjustments and/or biocide treatments can be regulated.

Drilling fluids also contain materials that can be biodegraded into corrosion accelerators with little effect on hydraulic properties. Plant and wood fibers are prime examples. It is reasonable to assume that corrosion probably is caused by micro-organism by-products in some drilling wells and that their control is desirable.

Practical control of micro-organisms can be accomplished if the pH can be maintained above 10, or if the fluid is saturated with a salt such as sodium chloride. However, because of the proliferous nature of micro-organisms in certain drilling fluids, biocides are needed for control. Chlorinated phenols or paraformaldehyde at concentrations up to 5.7 kg/m^3 are used in drilling fluids. These treatments can vary because the solids in drilling fluid usually favor the growth of micro-organisms and tend to reduce biocidal efficiency.

6.1.3.5 Electrochemical Factors

One form of corrosion by-product has been attributed to the flow of direct current in the corrosion cell. Electrochemical reduction of sulfur–oxygen groups results in hydrogen sulfide being formed at the cathode. This well-known corrosion cell reaction provides reactive hydrogen near the metal cathode surface. The hydrogen combines with the ever-present sulfur-containing compounds in drilling fluid to form hydrogen sulfide, which in turn may attack the steel.

6.1.3.6 Effect of Hydrogen

Hydrogen embrittlement resulting from exposure of steel to a wet environment at a moderate temperature has been a problem for many years. Surface corrosion initiates the attack, which is accompanied by the absorption of nascent hydrogen into the interior of the steel. This results in a reduction in the strength and toughness of the structure. The rate of hydrogen absorption is influenced by such environmental factors as contaminants, pH, and temperature.

Steel hardness (strength) determines the type of failure or damage to a given structure. Spontaneous brittle failure occurs in high-strength steel and blistering occurs in low-strength steels. Hydrogen embrittlement, recognized as a special problem, has resulted in limited use of high-strength steels in the petroleum industry.

Preconditions for hydrogen embrittlement are high-strength steel, stress, exposure time and environmental factors. Steels with yield strengths greater than approx. 551.2 MPa (80 000 psi) and hardness exceeding Rc 20 are susceptible to spontaneous brittle fracture. It is common to find steels of this strength and hardness in drilling and producing equipment.

6.1.3.7 Influence of Stress

Both residual and applied stresses increase embrittling tendencies. Continuous stress for a given time is required for this form of failure to occur, and under some conditions the metal may be purged of potentially damaging hydrogen from the interior of the steel.

Purging requires that hydrogen must be allowed to diffuse to the surface. Increased temperature is considered beneficial in facilitating movement of the entrained hydrogen through the steel lattice. Heat seems to have a dispersing effect and enhances the escape of hydrogen from the metal matrix, a beneficial effect that may be linked to the relaxation of bonds between metal atoms as the result of increased temperature.

6.1.3.8 Effect of Acid Gases

The acid gas contaminants (carbon dioxide and in particular, hydrogen sulfide) increase environmental embrittlement tendencies. Their effect is to increase the volume of hydrogen entering the steel by causing corrosion that supplies hydrogen ions and by interfering with cathodic reactions. Chemical treatments can be utilized to overcome some of these effects.

Chemical control of hydrogen embrittlement is usually difficult because environmental alterations will affect only one of the four basic conditions leading to this form of corrosion.

6.1.3.9 Effect of Alkaline Additions

Alkaline materials neutralize the acid formed by the gases and thus reduce the hydrogen absorption into the steel. Sodium or calcium hydroxide, or sodium carbonate are the primary materials used to increase and maintain a basic pH in drilling fluid. Film-forming amine-type inhibitors also are used against hydrogen embrittlement. These materials are known to affect the cathodic sites and tend to offset the detrimental effects of sulfide or other cathodic poisons. Amine-type salts that contain sulfur groups or triple-bonded components tend to be effective against embrittlement in drilling fluid environments. Oil muds (water in oil emulsion systems) are clearly recognized as a most effective defense against hydrogen embrittlement, as well as other forms of corrosion attack.

6.1.3.10 Use of Saturated Salt Solutions

Saturated salt solutions are commonly used both as drilling and packer fluids. Unsaturated salt solutions are believed to cause more severe corrosion than saturated fluids. Increased solubility of acid gases in the dilute solutions is the basic cause. Inhibitors are recommended for these solutions because corrosion is clearly a problem in highly conductive salt environments.

6.1.3.11 Oil Mud Drilling Fluids

Oil mud drilling fluids have been in wide use for a number of years. These fluids are composed of a continuous oil phase in which water has been emulsified. The emulsifying agents consist of organic soaps and amine-reacted compounds and are not only strong emulsifiers but also excellent corrosion inhibitors.

The water that is emulsified into the oil contains various salts, including alkaline materials. In a properly prepared oil mud, the water phase does not contact the drilling equipment. This type of

drilling fluid is stable to extreme pressures and temperatures encountered. Due to their electrical non-conductive properties, corrosion is not a problem.

6.1.3.12 Drilling Fluid Inhibitors

Inhibitors are used most often to remove or neutralize contaminants, or to form a film with relatively high dielectric strength on the equipment. Oxygen scavengers, such as sodium sulphite, are currently used in both water and oil muds. Calcium or zinc compounds are used to precipitate carbon dioxide or hydrogen sulfide. Alkaline materials are used in drilling fluids for both rhelogical control and corrosion inhibition.

Generally, pH is increased above that normally required for good fluid properties when corrosion inhibition is needed. Sodium hydroxide is the main chemical used for this purpose. As a rule, when corrosion rates are below 9.76 $kg/m^2/yr$ (2 $lb/ft^2/yr$) and uniform corrosion attack is occurring, pH control is all that is needed for effective inhibition.

If corrosion attack is localized or of the pitting type, then organic, film-forming inhibitors such as cathodic amine salts are strongly recommended. Some judgment is required in these inhibitor treatments. For example, previous pitting damage of the drilling equipment (drill pipe) should be taken into account.

Film-forming organic inhibitors are most effective when applied directly to the metal surface. Because they have the ability to displace water in surface pits and fatigue cracks, they are extremely useful in drilling fluid environments. Batch-type treatments are used to deliver the organic material to the exposed metals. This avoids mixing the inhibitor with the bulk of the drilling fluid. Film-forming inhibitors tend to be adsorbed on the solids in drilling fluids and thereby lose their effectiveness. For this and other obvious economic reasons, a batch method is recommended over continuous concentration-type treatments. Because some organic inhibitors are compatible with certain types of drilling fluids, a fixed concentration can be established for corrosion control. Such materials are primarily long-chain organic acid soaps, useful as torque reducers and extreme pressure lubricants. Their dual usefulness tends to justify the extra cost of continuous concentration-type treatment.

Organic inhibitors used to protect drill pipe in weighted, as well as in low-solids muds are effective when proper attention is given to the application method. Every effort should be made to apply the inhibitor to the drill pipe rather than to mix into the drilling fluids. This permits better control of drilling fluid properties and avoids excessive corrosion inhibitor costs.

6.1.3.13 Treatment Procedure

Establish corrosion rate and identify type of corrosion attack with drill string corrosion coupons prior to treatment. Each well should be evaluated individually and inhibitor treatments based on evaluation of the corrosion coupons.

Prepare a mixture of organic inhibitor with diesel oil or sweet crude oil in a separate mixing tank. The inhibitor–oil mixture can be varied from 1:6 to 1:13.

Example

For 378 liters (100 gallons) of a 1:13 mixture: 26.5 L (7 gallons) of inhibitor to 351 L (93 gallons) of oil. Because concentration and frequency of treatment will vary, better results will be obtained by establishing the proper treatment for each well. ■

When the inhibitor cannot be diluted with oil, it can be used in its concentrated form. Some organic materials are dispersible in water, which may be substituted for the oil.

Drill pipe in the hole should be filmed initially by adding 38 L to 76 L (1 to 2 barrels, 42–84 gallons) of inhibitor–oil mixture at the pump suction and pumping the batch around.

For maintenance treatment, batch 19 to 95 L (5 to 15 gallons) of inhibitor–oil mixture through the pump suction every 2 to 4 hours. If the corrosion rate is reduced and pitting or localized corrosion attack is not occurring, treatment frequency usually can be reduced.

After completion of the well, the drill pipe should be washed inside and out to remove all the drilling fluid and drilled solids. It should then be treated with inhibitor–oil mixture by spraying inside and out, or by dipping prior to storage on the rack.

Where corrosive conditions are severe, the inhibitor–oil mixture can be batched down the drill pipe during connections and poured into the annulus to film the drill pipe while making a trip.

This type of batch treatment is usually based on the rule of thumb: 5.7 L (1.5 gallons) of inhibitor–oil mixture for each 304 m (1000 feet) of drill pipe in the hole. Spray equipment has been designed to treat the drill pipe while making trips. This technique is preferred for coating the outside of the drill string.

A weighted (high-solids) drilling fluid is more abrasive than a low-solids fluid, and the solids will tend to erode the inhibito–oil film from the drill pipe. In this case, more frequent treatments are required. In a high-solids or viscous drilling fluid, the use of a water cushion directly ahead of the inhibitor–oil mixture can be beneficial. This cushion tends to clean the drill pipe to allow the inhibitor–oil mixture to reach and adhere to the metal surface more readily.

6.2 Production

Oil and gas fields consume a tremendous amount of iron and steel pipe, tubing, casings, pumps, valves, and sucker rods. Leaks cause loss of oil and gas, and also permit infiltration of water and silt, thus increasing corrosion damage. Saline water and sulfides are often present in oil and gas wells.

Corrosion in wells occurs inside and outside the casing. Surface equipment is subject to atmospheric corrosion. In secondary recovery operation, water may be pumped into the well to force up the oil.

6.2.1 Characteristics of Oil and Gas Wells

While there are many other ways to categorize oil and gas wells, this chapter considers them in the following broad categories:

- Oil well – that is, producing mainly liquid hydrocarbons
- Gas well – a well that produces fluids from a gas or gas-condensate reservoir
- Condensate well – that is, producing significant quantities of liquid hydrocarbons along with gas at high pressures and temperatures.

6.2.2 Oil Wells

6.2.2.1 Sweet Oil Wells

It appears that corrosion in high-pressure flowing wells that produce pipeline oil has become almost commonplace in many areas. Three methods are used to combat this corrosion as follows:

- Coated tubing
- Inhibitors
- Alloys.

Coated tubing has found most favor. Epoxy paints and powder epoxy coatings should be used.

6.2.2.2 Sour Oil Wells

These wells handle oil with higher sulfur contents than sweet wells and represent a more corrosive environment. In high- H_2S wells there may be severe attack on the casing in the upper part of the well where the space is filled with gas. Water vapor condenses in this area and picks up H_2S and CO_2.

Corrosion is reduced by inhibitors that are injected continuously or periodically depending on the well corrosivity.

6.2.2.3 Condensate Wells

Condensate wells handle fluids (gas containing dissolved hydrocarbons) at pressures up to 680 bars (10 000 lb/in^2). Depths run up to 4570 m (15 000 ft).

Carbon dioxide is the chief corrosive agent, with organic acids contributing to the attack. Approximately 90% of corrosive condensate wells encounter conditions as follows:

- Depth greater than 1500 m (5000 ft)
- Bottom hole temperature above 71 °C (160 °F) and pressure above 100 bars (1500 lb/in^2)
- Carbon dioxide partial pressure above (1 bar)
- Wellhead pH of less than 5.4.

The corrosion characteristics of a well are determined by:

- Inspection of surface equipment
- Analysis for carbon dioxide, organic acid, and iron
- Coupon exposure tests
- Tubing-caliper surveys.

Organic inhibitors available in oil-soluble, water dispersible, or water-soluble forms may be used to control corrosion. Determination of iron content and tubing-caliper surveys are used to measure the effectiveness of inhibitor treatment.

Substitution of medium-carbon manganese steels by alloy steels, and the use of stainless steel, monel, satellite, and copper-based alloys for valves and other wellhead parts for corrosion control are subject to the technical and economic evaluation of the subject.

6.2.3 Gas Wells

6.2.3.1 Sweet Gas Wells

With regard to CO_2 corrosion alleviation in flow lines, there are several choices, as follows:

- Low-alloy steel with a corrosion allowance can be used.
- Use of corrosion-resistant materials, alloy, or coating. With regard to CO_2, either type 316 stainless steel or duplex stainless steel will provide sufficient internal corrosion resistance. If H_2S is present, then NACE MR-01-75 must be followed.
- Internally line low-alloy steel pipelines with a corrosion-resistant material.
- Use of non-metallic pipe materials.

6.2.3.2 Sour Gas Wells

If the partial pressure of H_2S is greater than 0.34 KPa (0.05 psia) the gas stream is sour and materials that resist sulfide stress cracking must be used. The latest revision of NACE MR-01-75 lists materials that are recognized to have acceptable resistance to sulfide stress cracking.

6.2.4 Offshore Production

Offshore production presents many interesting corrosion problems. Platforms are built over the water and supported by beam piles driven into the ocean floor. Each beam is surrounded by a pipe casing for protection. Similar platforms are used far out at sea for radar towers.

A variety of corrosion prevention methods are used in such structures, some of which are beyond the scope of this book. The corrosion prevention methods include:

- Adding inhibitors to the stagnant seawater between beams and casings.
- Cathodic protection, with sacrificial anodes or impressed currents, of underwater structures.
- Paints and other organic coatings to protect exposed structures above the splash zone.
- Monel sheathings at the casing splash zone. This portion of offshore structures is the most susceptible to rapid corrosion.

6.3 System Requirements for Corrosion Control of Oil Fields by Inhibitors

Before a corrosion prevention procedure using inhibitors can be implemented, the system requirements should be clearly understood. The following problem areas and parameters will dictate the requirements and performance specifications of a particular inhibitor.

6.3.1 Pipelines and Flow Lines

6.3.1.1 Top of Pipe

The 12 o'clock position in a line is the most difficult part to inhibit. Where the flow velocity is less than required for turbulent flow, liquids will not contact this area except in areas of slug or partial slug flow. Addition of a volatile component to the inhibitor may be required.

6.3.1.2 Water-Wet Area: Bottom of Pipe

In most cases, free liquid moves along the bottom of the pipe. Depending upon the velocity, the layer may be both condensate and water, or discrete layers of oil and water. At low velocities solids dropout can cause concentration cells and pits underneath the deposits.

6.3.1.3 Turbulence-Prone Areas

Areas downstream of welds, minor buckling of the line, low spots, and solids deposits can increase shear stress and turbulence, which may aggravate corrosion. Low spots cause slugs of liquid at intervals. Turbulence removes protective scale, aggravates abrasion and erosion if solids are present, and may affect inhibitor performance by removing the film. Inhibitors must be able to withstand the shear stresses.

6.3.2 Production Systems

6.3.2.1 Tubing

Protection of production tubing requires that the inhibitor be squeezed, added continuously, or have film persistency so that batch treatment is feasible. Shear stresses impose the same requirements on inhibitors to withstand velocity effects. The tubing will be wetted more completely on the low side

in deviated (non-vertical) wells, and in low-volume producers a separate a layer of water on the low side may be the only corrosive area.

6.3.2.2 Down-Hole Pumps

In rod-pumped wells, abrasion of rods on tubing adds the requirement that the inhibitor film have some lubricating properties. In many wells entry of air through the annulus requires that the inhibitor function in the presence of oxygen. Down-hole centrifugal pumps are susceptible to failure due to scaling, and to velocity effects.

6.3.2.3 Surface Equipment

Problem areas include well heads, chokes, and vessels where velocity effects are substantial, and separators and other vessels where stagnant areas, scale, and solids deposits can create concentration cells. Growth of bacteria may occur in these areas.

6.3.2.4 Injection Systems

Secondary recovery (water-flooding), and tertiary recovery using CO_2 micellar fluids and polymers introduce some specific requirements. Inhibitors must have proper solubility and wetting characteristics and be able to perform in the presence of the surfactants and polymers added to the flood. A surfactant component may be required in the inhibitor to maintain injection rates in produced water injection systems.

6.3.2.5 Gas/Liquid Composition and Operating Conditions

The major controlling factors for corrosion rates are the composition of the gases and liquids produced or transported, and conditions of flow, temperature, and pressure.

6.3.2.6 H_2S and CO_2 Contents

The acid gas content determines the type of corrosion and greatly influences the corrosion rate. Corrosion rates are directly related to the amount of CO_2 dissolved in the water, which determines the amount of carbonic acid and subsequent metal dissolution. If organic acids are present the corrosion rate is increased by removal of bicarbonate ions, and by dissolution of protective ion carbonate:

$$CH_3COOH + HCO_3^- \rightarrow CH_3COO^- + CO_2 + H_2O \tag{6.1}$$

$$2CH_3COOH + FeCO_3 \rightarrow Fe(CH_3COO)_2 + 2H^+ \tag{6.2}$$

High velocity causes turbulence and increases corrosion rates. The temperature of the system, increased salinity, and bicarbonate content also affect the corrosion rate and the inhibitor requirements.

Where H_2S is present, line failures due to penetration underneath pits can occur in a short time. The sulfide film formed may be anodic to the metal surface, and afford some degree of corrosion protection. In many cases, however, the layer of FeS is not continuous and if so, may be porous. The net result is pit formation and growth. Sulfide stress cracking and hydrogen embrittlement are also factors to consider in inhibition for H_2S. In systems where H_2S and CO_2 are both present, the ratio of CO_2 to H_2S determines whether CO_2 or H_2S corrosion mechanisms will dominate. Inhibitors should be effective against both H_2S and CO_2.

6.3.2.7 Liquid Composition

Water composition may range from water of condensation to high-salinity formation water. Inhibitor solubility and dispersibility requirements will be affected. Water floods range from seawater to

mixtures of reinjected produced water with surface and well water. In some cases fresh produced water is discharged into streams, so environmental requirements are of concern.

Hydrocarbons may range from low molecular weight aliphatics to high molecular weight asphaltenes. Condensate usually does not enhance inhibitor filming, while higher molecular weight hydrocarbons and organic compounds may help the inhibitor. Paraffins and waxes form deposits and require treatment.

6.3.2.8 Temperature

Carbon steel corrosion by CO_2 is directly dependent upon temperature. At temperatures below 60 °C scale provides little corrosion protection. In the temperature range of 60 to 100 °C, iron carbonate will form. The scale may result in lower than predicted corrosion rates, but severe pitting can (and usually does) occur.

At temperatures above 100 °C scale is formed on the surface as a thin, dense layer of iron carbonate/magnetite, and affords good corrosion protection under most conditions.

Temperature affects the inhibitor requirements as far as stability and filming ability is concerned. No polymerization of the inhibitor can be tolerated, since plugging can take place.

6.3.2.9 Pressure

Pressure has a direct effect since corrosion rates are proportional to acid gas partial pressures. It will affect inhibitor solubility as, at extremely high pressures, methane will act like a liquid and may remove the inhibitor, leaving a thick residue.

6.3.2.10 Flow Parameters

The flow parameters to consider are velocity, type of flow, and gas to liquid ratio.

Velocity has definite effects on the ability of inhibitors to control corrosion. The type of flow is determined by velocity, and is characterized as annular, stratified, or slug flow. Flow regimes vary in different sections of lines and tubing, because of restrictions, and low places. Slug flow in producing wells increases turbulence.

Distribution of the inhibitor in all areas of a pipeline is related to flow velocities and the composition of the gases and liquids in the line. At annular flow velocities, the stream is homogeneous, and inhibitor added continuously will contact all portions of the line equally.

When flow velocities are lower, the flow is partly annular, with a higher concentration of liquids in the bottom half of the pipe, i.e. the film of liquids is thicker. Lower flow velocities allow some free liquid to collect in the bottom of the line, and slug flow predominates. As the flow rate declines, stratified flow predominates and the stream has separate gas and liquid phases. The top portion may not be regularly contacted at all by liquid, except that condensed from the gas. A vapour-phase inhibitor or some means of introducing a periodic batch that contacts the top of the line should be considered. In stratified flow, partitioning of the inhibitor between oil and water layers is important. Slug flow increases requirements for the ability to withstand shear stress.

At velocities of less than 10 m/s it is reported that very little effect on CO_2 corrosion rates will take place. At velocities of 10 to 20 m/s, turbulence can cause local areas of higher attack, and at velocities above 20 m/s corrosion by-products will be removed. This increases corrosion rates and could affect inhibitor filming ability.

6.3.3 Other Factors Affecting Corrosion Inhibitor Requirements

Other factors affecting corrosion include bacteria, scaling, mechanical or chemical treatment of lines prior to commissioning, such as treatment of the pipe during storage, and completion methods and

treatment procedures. The economics of treating is important. Compatibility of the inhibitor with scale inhibitors, oxygen scavengers, and biocides imposes special requirements.

6.3.3.1 Bacteria

Bacteria, particularly sulfate reducers, can increase corrosion rates and may need to be controlled with organic biocides. Organisms may be introduced during hydrotesting of lines, and by contamination of producing systems from sumps and seawater flushing of vessels.

6.3.3.2 Scale

Scaling may need to be controlled to prevent pitting corrosion. The inhibitor may be a combination material or a scale inhibitor may be used separately.

6.3.3.3 Mechanical and Chemical Pretreatment

Pipelines may require treatment to remove mill scale and deposits prior to a successful inhibitor treatment regime, and will be hydrotested. Prevention of corrosion and bacterial growth during testing is required.

6.3.3.4 Completion Methods and Treatment Procedures

Completion methods dictate the treatment procedures. If the well is flowing with a packed-off annulus it may be necessary to install a chemical string for continuous treatment. Side pocket mandrels with chemical injection valves or capillary strings require that inhibitors be stable in the annulus or the string for extended periods.

If a chemical string is not feasible, batch treatments using persistent film inhibitors may be used. The inhibitor is designed to form a tough film that is not too soluble in the production stream so it will last for a sufficient time between treatments. The batch may be displaced with liquids, gas, or nitrogen. Squeeze inhibitors must be designed to be stable in the formation, and not cause severe emulsion problems. The adsorption characteristics should be controlled for proper feedback of the inhibitor. Pumped wells, can be treated by continuous addition or batching down the annulus.

6.4 Types of Inhibitor

The most important type of inhibitor to the oil industry is the filming inhibitors. One end of the inhibitor molecule is adsorbed onto the metal surface. The non-polar tail of the inhibitor molecule is oriented in a direction generally vertical to the metal surface. It is believed that the hydrocarbon (non-polar) tails mesh with each other in a sort of "zipper" effect to form a tight film that repels aqueous fluids, establishing a barrier to the chemical and electrochemical attack of fluids on the base metal. A secondary effect is the physical adsorption of hydrocarbon molecules from the process fluids by the hydrocarbon tails of the adsorbed inhibitor molecules. This increases both the thickness and effectiveness of the hydrophobic barrier to corrosion.

Based on the above explanation, it may be understood why such inhibitors are generally more effective in the presence of an oil phase. In fact, it is often difficult to use filming inhibitors effectively and economically in its absence.

Filming inhibitors are available in a wide variety of formulations and solubility characteristics. The question of whether to use an oil-soluble or a water-soluble inhibitor is somewhat arbitrary. Some operators prefer to use a water-soluble or water-dispersible inhibitor when the water to oil ratio of the producing well is greater than one. Other operators hold an opposing view, preferring to build a high concentration of oil-soluble inhibitor in the lesser phase. In practice, both methods have been

shown to be effective, leading to the conclusion that the gross physical properties of the inhibitor are less important than getting good circulation of the inhibitor through the system. The type of inhibitor must be selected on the basis of the individual system.

Vapor-phase inhibitors are added as gases or volatilize from a liquid inhibitor. In boilers, volatile basic compounds such as morpholine or ethylenediamine are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide. In gas lines, the volatile inhibitor is present in the gas phase, separate from any liquid in the line. Compounds of this type inhibit corrosion by making the environment alkaline.

Oxygen scavengers are added to water either alone or with a corrosion inhibitor. Organic corrosion inhibitors alone in aerated brine water will slow general corrosion, but will not always prevent pitting attack. The most common oxygen scavengers used in water at ambient temperature are sodium sulfite and sulfur dioxide.

The effectiveness of film-forming inhibitors, as already stated, depends upon strong adsorption of inhibitor molecules on the metal surface to be protected. Clean up, consequently, is very important in the control of corrosion. Some corrosion inhibitors have the ability to clean by nature of their makeup or with the aid of added surfactants. These surfactants actually remove oil-coated corrosion products, allowing the inhibitor to attach itself to the clean metal. It should always be borne in mind that without proper clean-up, control of corrosion is generally unsuccessful.

6.5 Selection of Inhibitor

A system must be carefully examined before a program of corrosion inhibition can be planned effectively. The examination must include a survey of any adverse effects an inhibitor may have on the process. The most likely adverse effects are foaming, the formation of an emulsion, and loosening of scale.

The test for foaming should be performed. Most corrosion inhibitors cease to function at a pH below 3. Normal film-forming organic inhibitors of the water-soluble type have an upper temperature limit of 140 °C (300 °F), while oil-soluble inhibitors have a limit of 196 °C (385 °F), when cooled the inhibitor is active again, so it is not destroyed if the temperature is not too high.

Watch for inhibitors that polymerize at higher temperatures. Also be aware that the evaporation of solvent carrying the inhibitor can leave the inhibitor as a "gunk" in the well. In treating dry gas wells, this can be minimized by using a solvent that has a considerably higher boiling point than the condensate produced by the well.

For most applications it is desirable to use an inhibitor that is insoluble, but dispersible, at a 10 to 25% concentration in the hydrocarbon diluent, which may be distillate, aromatic solvent, crude oil etc. The inhibitor will film from the liquid onto the metal surface. Care must be taken that the inhibitor is not tied up as the inner phase of a water emulsion. The inhibitor has difficulty breaking from a dispersion of this type.

Remember that a corrosion inhibitor program is basically a coating treatment. The amount of inhibitor required depends upon the amount of metal to be protected, not upon the volume of fluid produced by the well. The amount of fluid produced determines the frequency of treatment, although it is probable that no well should go longer than three months between corrosion treatments.

Most wells are probably over-treated initially, with the time until the next treatment too long. For instance, a well 1800 feet deep, producing 8 m^3 (50 barrels) of oil and 300 m^3 of water daily may be treated every six months for corrosion with one drum of chemical.

This is poor, since 37.8 dm^3 (10 gallons) of chemical would treat the well with the other 0.15 dm^3 (40 gallons) wasted. The treatment, if corrosion is not too severe, will last from 30–60 days, leaving the well exposed to a corrosive environment for four to five months. A treatment using less chemical on a more frequent basis is more successful than a larger treatment at too long an interval.

When setting up a corrosion inhibitor program, it is necessary to learn:

- Where corrosion is occurring
- How inhibitor can be applied to this area
- How fast the corrosion is occurring
- How much oil, water, gas, and condensate are produced per day
- If the fluids are the sweet or sour
- If oxygen is present?
- The size of the tubing, how deep is it, the bottom-hole temperature and pressure.
- What has been done in the past; what worked, what failed
- How the operator prefers to treat.

For the final selection, running tests should be performed in order to choose the best inhibitor(s).

6.6 Measurement

Several tools are available to determine if a well is corrosive or if a corrosion treatment is effective. Among these are:

- Equipment failure records
- Instruments such as hydrogen probe, corrosometer, corrater, pirameter, galvanic probe, and oxygen meter
- Oil and water production data
- Coupon surveys
- Caliper surveys
- Well and flow line inspections
- Manganese count
- Amine residual.

Iron counts, or more precisely, the dissolved iron concentration in the water, can be one of the best methods of monitoring corrosion in sweet systems depending on system characteristics. Iron count data are no better than the technique used in obtaining and analyzing the sample. Samples taken at the wellhead are usually superior to all others. In addition, because of their detergent action, many inhibitors often cause an initial increase in the amount of sludge and scale going into the process stream, as oil deposits are loosened by the detergent-inhibitor and slough-off equipment. This increase must be recognized for what it is and not be assumed to signify an increased corrosion rate.

Several precautions should be taken to assure good results:

- Determine if there is any "natural" iron in the water. Some formation waters naturally contain from a few to very high ppm iron, even when no corrosion is occurring.
- Of primary concern is the amount of iron dissolved in the water in systems containing little or no oxygen. This means a single speck of solid corrosion product can lead to incorrect results. It is advisable to filter the sample to remove any suspended solids. Also, exposure of the water to air will cause all of the dissolved iron to precipitate as ferric hydroxide, $Fe(OH)_3$ Therefore, good iron counts should be run on samples immediately after sampling, or the sample acidified with hydrochloric acid to prevent precipitation.
- Iron counts in systems that are thoroughly aerated or which contain H_2S are of limited value unless the pH of the water is below 4. If carbon dioxide is present, the pH may be low enough to prevent the precipitation of iron as iron hydroxide.

Properly installed coupons are excellent for monitoring corrosion. They are not very successful in pipeline programs because they need to be installed in places that are generally not easily accessible.

Offshore pipelines often have coupons installed both at the bank and on the platform, at the inlet of the system. The coupons on the bank are of little benefit because most of the corrosion has occurred before the fluids reach the bank; thus, the corrosive gases are no longer present. The coupons at the inlet are located upstream of water fallout so there is no stagnant liquid area that is constantly replenished with corrosive gases.

Manganese is sometimes found in produced water, making it difficult to use dissolved manganese as a method of monitoring corrosion, except to determine change in concentration between the entrance and the exit of a system.

Some comment should be made about "oil and water production data." In the history of each oil field it can be observed that corrosion and the ratio of produced water and oil are closely tied together. The production becomes corrosive only after passing a certain critical point in water and oil production. Although wide variations in this critical ration exist from field to field, narrow limits usually apply to a single field. This "rule" does not apply to condensate wells, which can be corrosive from the time of completion.

Inhibitor residuals are occasionally used to monitor corrosion control programs. By knowing at what concentration certain water soluble inhibitors give protection, we can generally tell if protection is being accomplished.

Caliper surveys are not recommended for pipe that has been protected with a corrosion inhibitor. The caliper leaves marks on the pipe where the inhibitor is scraped off; these scratches then corrode. A caliper can be run while the tubing is filled with inhibitor.

6.7 Factors Governing Oil Well Corrosion

Most crude oils are non-corrosive and as long as well bore and surface equipment are in an oil-wet condition the production system is protected. This condition will persist as long as oil remains the external phase of the produced liquids. The phase relationship between the oil and water will generally invert between a cut of 25–35% so that water becomes the continuous phase.

With the inversion the well bore equipment will change to a water-wet condition. The time required for equipment to become water-wet is a function of the tenacity and thickness of the oil film. However, once the phase inversion has occurred, eventually the system will become water-wet.

It is suggested when the cut approaches 25% analyses be reviewed or tests conducted to evaluate the potential corrosivity of the wells. In most production areas waters from the same formation will be roughly comparable as to corrosivity. Also where the produced gas contains either hydrogen sulfide and/or carbon dioxide, it should be anticipated that the produced water will be corrosive.

The installation of corrosion coupons (corrcoupons) at this time is highly desirable. If significant corrosion occurring, the coupon will give an indication of severity. After a corrosion program has been started a comparison of "before and after" results are a measure of the treatment effectiveness.

A step-wise procedure can be followed in evaluating the corrosive possibilities in a well. With produced waters having a pH of 6 or lower, serious corrosion is inevitable once the system becomes water-wet. If the pH ranges between 6.0 and 7.0 corrosion will also occur once the water becomes the external phase and inhibition would be desirable when the attack is of the pitting type or over 0.127 mm/yr (50 mpy).

In using this approach it is imperative that the pH measurements be on freshly produced samples as soon after being withdrawn from the system as practical. The order of magnitude rather than a high degree of precision is the principal requirement of this measurement; data obtained from pH paper is quite adequate.

Where samples are transported to a laboratory or stored for any significant time (one or two days) the pH will not be representative. In cases where this type of measurement is the only one available and the pH is below 7.0 it is suggested that the measurement be lowered by 1.0.

Another factor frequently overlooked in corrosion inhibition programs is the changes that occur in the production characteristics of the wells during primary depletion or in secondary recovery periods. Chemicals and treating methods that give good protection during the period when the water cuts are relatively low (25 to 40%) are frequently inadequate when large volumes of water are produced. It is highly desirable to begin a systematic monitoring program at the same time an inhibition program is started. This, in addition to establishing the success of the program, will usually indicate when a change in chemicals for application method is necessary.

One condition that is often neglected in oil well corrosion programs is the possibility of air entering the system. Occasionally wells are maintained in a pumped off condition with the annulus open. In the later stages of depletion, with high water cuts and no significant gas, air can contaminate a system through the open annulus. Other sources of air are polish rod stuffing boxes, and valve packing on the well side of the flow-line check valves. In this case, it is presumed that the systems are air-tight and all corrosion is from the produced fluids.

There are generalities that can be used in a preliminary evaluation of the possibility of corrosion in a specific oil well or field, and treatment conditions that can be considered when no other information is available. Some of these "rules of thumb" are given below:

- In wells producing less than 25% water, the equipment will be oil-wet and corrosion would not be anticipated.
- In wells producing 25–40% water, the equipment may be either oil- or water-wet, and the possibility of corrosion depends on the corrosivity of the water.
- In wells producing over 45% water, the equipment will be water-wet and corrosivity will depend on the corrosivity of the water.
- When the equipment is water-wet and the pH is between 6.5 and 7.0, mild corrosion is probable, but unless it is a pitting-type attack, frequent equipment failure would not be expected.
- When the equipment is water-wet and the pH is between 6.0 and 6.5, significant corrosion is occurring and further tests are required to determine how serious the attack may be.
- When the equipment is water-wet and the pH is below 6.0 serious corrosion is occurring and an inhibition program should be started.
- When equipment inspection or coupon data indicate a pitting-type attack, the corrosion should be considered serious regardless of mmy (millimeters per year) and an inhibition program should be started.
- Where applicable, an oil-soluble, water-dispersible inhibitor should be used.
- Where applicable a periodic batch-treatment procedure is preferred.
- A treatment rate of 10–15 ppm should be used for mild corrosion.
- A treatment rate of 15–25 ppm should be used for moderate corrosion.
- A treatment rate of 25 + ppm should be used for serious corrosion.
- Initial treatment should be on a weekly basis and extended as monitoring indicates.

The phase relationship of water in oil will invert between 25–40% water. After inversion, equipment will be water-wet and corrosion may occur. The following is suggested as one procedure for early detection of corrosion:

- Corrosion occasionally occurs above a pH of 7.
- When equipment becomes water-wet corrosion will occur. Maintain a planned monitoring program.
- Check systems for air entrainment; if found, eliminate and retest.

Frequently iron counts are used as a means of monitoring corrosion and the effectiveness of inhibitor treatments in gas wells. Interpreting iron counts without supporting data can be misleading. In order to properly assess iron counts the chloride content, rate of water production, and information as to hydrogen sulfide or carbon dioxide content of gas is necessary.

Table 6.1 *"Rules of thumb" to use in interpreting factors governing oil well corrosion*

Water production (L/1000 m^3)	Chloride content (ppm)	Remarks
56–168	0–250	Water primarily condensed from gas as pressure and temperature. Changes in tubing: corrosion will occur principally in upper parts of tubing (0–900 m) and in the well head. If CO_2 is present, corrosion can be quite severe in zones of high turbulence, with marked localized pitting; with H_2S, corrosion will be of a more general type. Iron counts up to 150 usually are not of concern, providing proper metallurgy has been selected for the well head.
168–280	250–500	Water production is now a combination of formation and condensed water with corrosion possible over the entire tubing string and well head. With CO_2 or H_2S, severity is approximately the same as above. Iron counts of 50 to 150 are acceptable, providing proper metallurgy has been selected for the well head.
280+	500+	The water is not primarily from the formation; corrosion will occur over the entire tubing string and well head.With only trace amounts of CO_2 and H_2S, severity will decrease with increasing water production. However, inhibition may become more difficult due to the tendency of water to desorb or wash the inhibitor film from equipment. Iron counts of 50 or less are desirable with permissible count decreasing as water increases.

Table 6.1 lists the "rules of thumb" to use in interpreting data.

Whenever possible, a base iron count on formation water should be obtained. Produced water can contain significant amounts of iron in solution. This should be deducted from iron count data before applying the above criteria. Where base iron counts are not possible, a number of iron counts should be obtained prior to inhibiting the well. The reduction in count after treatment can then be used as a base.

6.8 Application of Inhibitor

Unless otherwise specified by the supplier of the inhibitor, the following procedures should be performed.

6.8.1 Gas Condensate and Flowing Oil Wells

Wells of these types are squeezed, displaced, batch treated, and continuously injected.

6.8.1.1 Squeeze

Squeeze treatments are made by mixing the selected inhibitor in oil, aromatic solvent, or water at the proper ratio, which is determined by inhibitor fall out. The inhibitor may not be totally soluble in the diluent, but must be dispersible enough to be carried by the fluid into the tubing and down hole. The mix is pumped into the tubing and displaced to the bottom, followed by sufficient fluid to

over-displace the mixture into the formation. It is advised to shut the well for two to four hours after the squeeze is completed and to bring the well on-stream slowly.

Wells with low bottom-hole pressure cannot withstand the hydrostatic head. They can be treated the same as above, however, except the inhibitor–diluent mix is atomized with nitrogen and then displaced and over-displaced with nitrogen. Squeeze treatment with nitrogen is costly because of the equipment required. It may be possible to use high-pressure natural gas for the squeeze instead of expensive nitrogen.

It should be borne in mind that the squeeze treatment can damage the oil well. Loosely consolidated sand will move and is worse when the flow is reserved. Squeezing this type of well brings the loose sand into the flow channels and into the well. The use of fresh water should be avoided with formations containing clay this will cause the clay to swell.

6.8.1.2 Tubing Displacement

Tubing displacements are handled the same as squeezes except there is no over-displacement. One drum of the inhibitor mixed in the displacement fluid is added and the well is left shut in for about three hours after displacement is accomplished. The total volume of fluid-spearhead plus displacement should be only sufficient to displace to the bottom of the tubing. If the fluid level tends to drop, or the well goes on vacuum, the liquid will collect in the hold beneath the tubing instead of being sucked into the formation.

A special type of inhibitor in accordance with the supplier's recommendation should be mixed with the spearhead to minimize the possibility of blockage, should the treating fluid be sucked into the formation. This inhibitor should also be used in the displacement fluid to prevent the production of an emulsion when the fluid is returned.

6.8.1.3 Batch Treatment

Batch treatments are similar to the above two, except displacement fluid is not added to the tubing. The diluted inhibitor is pumped in, leaving the well shut in long enough for the mixture to fall to the bottom if no water is present in the tubing or to the oil–water interface if water is present. The well is then brought back slowly. In cases such as offshore where inhibitor dilution is not possible, batches have to be used "neat." This becomes a serious problem because restrictions (storm chokes, ball valves, etc.) stop the fall of the inhibitor as it attempts to get through the small opening and leaches out solvent.

The increased viscosity causes the inhibitor to fall slowly and to leave an uneven coating on the wall of the tubing. Some of the inhibitor that stays above the restriction eventually "gunks" prediluted inhibitors being used. In some cases where the restriction is close to the surface, a batch of hydrocarbon is used to push the inhibitor through.

6.8.1.4 Continuous Injection

Continuous injection is generally the best method, if it can be applied. Inhibitor is always present to repair places where the "old" inhibitor has been removed. Some wells are completed with parallel strings, concentric strings, and U-tube-type strings. If the well will support the column of inhibited fluid (parallel and concentric completions), then continuous injection can be accomplished. In most cases, a U-type completion will have a back pressure valve toward the bottom of the small string and can be loaded with the inhibited fluid.

In some cases, down-hole injectors are used; these are generally located in the packer. The annulus is loaded with the inhibited fluid and pumped in at the surface at the desired rate. The pump must have a sufficient output pressure to overcome the down-hole pressure (taking into consideration the hydrostatic head) to open the injector.

6.8.1.5 General Criteria

Wells in high-pressure oil or gas zones are often completed with a packer between tubing and casing so there is no communication with the surface except through the tubing. These wells may be producing oil and water plus gas or they may produce only gas. The inhibitor treatment method is dependent on what is in the tubing when the well is shut in.

If this is a gas well making little or no fluid (5.6–11.2 liquid m^3/Mm^3 gas) the shut in condition will leave the tubing full of gas. This well can be batch treated by pumping diluted inhibitor into the tubing. The volume of the treatment will vary from 18.926 to 37.75 liters of inhibitor in 158.9 to 749.85 liters of diluents, to one drum of inhibitor in 0.1589 m^3 to 1.589 m^3 of diluent, depending on whether the corrosion is known to occur near the surface or near the bottom of the well.

Weighted inhibitors are not recommended; wells of this type are best treated by tubing displacement or squeeze. When a gas condensate well is shut in, the water that collects in the tubing generally runs back into the formation, leaving only gas and condensate in the tubing. Trying to treat with a weighted inhibitor may not work because the water has disappeared.

Inhibitors for batch treatment or tubing displacement in gas wells are returned to the surface cut with water and distillate. The inhibitor concentration is high, and at high concentrations some inhibitors behave as good emulsifiers for water and oil. For this reason the inhibitors recommended for gas wells contain emulsion breakers to prevent emulsions that cause trouble in separators.

If a well is a flowing oil well making mostly fluid (oil and water), the shut in conditions will leave considerable fluid in the tubing. This well is best treated by a tubing displacement or squeeze if the bottom pressure is sufficient to return the injected fluids. This type of well can also be treated with weighted inhibitors.

The weighted inhibitor should be pumped or lubricated into the tubing and allowed to fall through the oil and water in the tubing. The well should remain shut in as long as possible after injecting the inhibitor to allow it to fall into the rat hole; no flush should be used.

6.8.2 Gas Lift Wells

Gas lift wells are treated by the four methods described above. The batch is generally accomplished with a weighted inhibitor because of the high water level encountered. The weighted inhibitor should be selected on release rate. Gas lift wells should be treated by squeeze if the corrosion occurs below the operating valves.

Some gas wells are completed with a macaroni string, a kill string, or a bottom-hole injector valve in a packer that permits communication from the surface to the bottom of the well. Wells completed in this manner can be treated by batch or continuous injection through the kill string.

Gas lift wells are sometimes treated by injecting the inhibitor with a chemical pump into the lift gas line. This inhibitor gives protection only from the operating valve to the surface. For this kind of application continuous injection-type inhibitors or batch-type inhibitors are effective. It is best to inject at the well, but injecting at the compressor is also possible.

The compressed gas will be distributed to a number of wells. In these cases it becomes necessary that both closest and farthest wells from the point of chemical injection be monitored closely. This shows whether good inhibitor distribution throughout the system is being obtained.

6.8.3 Pumping Wells

Total production from a well is the basis for calculating the ppm of chemical to be added; treatment should not be based upon oil production alone. The initial treatment should be several times greater in concentration than subsequent periodic treatment. The batch is pumped into the annulus; it must be followed by flush, generally with well fluids from the flow line.

The amount of flush should be 158.9 to 145.2 liters, depending on the height of annulus fluid above the pump; 159 liters (one barrel) of flush is adequate if the well pumps off daily, 795 liters (five barrels) is generally adequate for 30.45 m of fluid above the pump, and 175.2 liters is adequate up to 152.4 m of fluid above the pump.

The height of fluid in the annulus can be determined by instruments such as the echometer. A water-soluble dye added to the flush water can be used to determine how quickly the treatment chemical reaches the bottom of the well.

If large flush volumes cannot be used because of high annulus pressure, then batch treatment with conventional inhibitors is not recommended; weighted liquid inhibitors should be used. Treatment with weighted inhibitors is also recommended for very high fluid level wells and for wells that produce out of the casing. Weighted inhibitor application is as follows: The casing is flushed with 158.9 liters of well fluid and weighted liquid is pumped or lubricated into the annulus. The casing is left shut in for four to twenty-four hours. There should be no flush behind a weighted inhibitor.

Reda pumps have been treated with weighted inhibitors. The bottom portion of the Reda is generally in water. Since the impeller of the Reda is in the top section, the bottom is not protected by inhibitor treatments through the annulus. Weighted inhibitors that fall to the bottom of the rat hole will protect the pump.

Long or extended period batch treatments are occasionally performed on wells producing low water cut fluids (0 to 25% water). Oil-soluble or nearly oil-soluble inhibitors may be batched into the annulus. Usually half to one drum of chemical is used. The well fluids are circulated for two to four hours to mix the inhibitor into the annulus oil. The wells are then produced for a period of time (one month), when 37.8 to 56.7 liters (10 to 15 gallons) are again batched and the well circulated for two to four hours. With high fluid level wells this treatment has lasted for up to three months per batch. This procedure is a general guideline and the exact procedure should be supplied by the manufacturer.

6.8.4 Gas Pipelines

Pipeline inhibition is accomplished after clean-up by mixing an oil-dispersible inhibitor with hydrocarbon and batching between two pigs, using the formula proposed by the supplier. In wet gas systems a continuous injection-type method should be used, at an economical rate specified by the supplier, depending on the severity of the problem and the amount of water being handled.

Continuous injection is used after clean-up and batch treatment has been accomplished. In dry gas systems handling condensate, the same programs apply. Condensate should always be considered to contain some water. In dry gas systems that handle no liquids, clean-up and batch treatments are recommended. Continuous injection is not desirable because there is nothing to help carry the inhibitor down the line. Pipeline programs have to be designed for each system separately.

Gas gathering lines will generally have water collected in the bottom portion of the pipe on uphill slopes. Corrosion is bad at these spots. All of the surface of the pipe is probably water-wet and is subject to corrosion at a slower rate. Even those gas gathering lines that have separators and small glycol units at the well head generally contain some water. The H_2S or CO_2 produced by the gas wells is still in the gas, of course, so that it must be considered to be corrosive.

Corrosion inhibitor should be injected downstream of the separator or glycol unit, or at the well head if neither of these is used. Most of the liquid in the lines, and the corrosion inhibitor, will be removed by the separator and the filter at the gasoline plant, but some will always come through as a mist to the sweetening towers.

The sweetening towers will use MEA, DEA, sulfinol, or liquids of this type. Always test the corrosion inhibitor that is being considered with the liquid being used for sweetening, to determine if foaming will occur or emulsions form.

Hydrogen probes should be used in lines to monitor corrosion. These probes should be located where any liquid in the line contacts the probe; otherwise they are sensing the "corrosion" in the gas

phase. If the probe is in the gas phase, a water mist is carried by the gas, and the company relies on the reading of the probe, a vapor-phase inhibitor must be used.

6.9 Water Flooding and Water Disposal

The main hazard encountered in shifting from primary production to secondary recovery is in the possibility that foreign materials may be introduced into the production system. From a corrosion standpoint, the most important of these materials is oxygen.

Oxygen is rarely present in primary production environments below a few hundred meters. Oxygen may be present in make-up water if the water comes from sources open to the atmosphere (rivers, lakes, the ocean, or even some source shallow wells) or it may enter the system through vents in storage tanks, along the shafts of the suction side of centrifugal pumps or even through such equipment as diatomaceous earth filters.

Acidity in injection water is possible when produced water (water produced from the formation along with the oil) is used for flooding. This acidity is generally caused by residual acidic gases (carbon dioxide or hydrogen sulfide), but also may be due in part to low molecular weight organic acids.

If the waters handled contain hydrogen sulfide, or are acid with pH values below 6.5, or contain oxygen, they exhibit corrosive tendencies and need to be treated to reduce maintenance costs resulting from corrosion.

6.10 Transportation and Storage

Petroleum products are transported by tankers, pipelines, railway tank cars, and tank trucks. The outside submerged surfaces of tankers and the outside surfaces of underground and underwater pipelines are protected by coatings and by using cathodic protection. Cathodic protection is also applied to the inside of tankers to prevent corrosion by seawater used for washing or ballast.

Gasoline-carrying tankers present a more severe internal corrosion problem than oil tanks because the gasoline keeps the metal too clean. Oil leaves a film that affords some protection. Tank cars and tank trucks are coated on the outside for atmospheric corrosion.

Internal corrosion of storage tanks is due chiefly to water, which settles and remains on the bottom. Coatings and cathodic protection should be used. Alkaline sodium chromate (or sodium nitrate) is an effective inhibitor of corrosion for domestic fuel oil tanks.

Internal corrosion of product pipelines can be controlled with linings and inhibitors (a few parts per million) such as amines and nitrites. Ingenious methods for lining pipelines in place underground have also been developed.

Internal corrosion of sour gas pipelines should be controlled by suitable inhibitors that are injected continuously or periodically, depending on the type of inhibitor.

6.10.1 Corrosion Control by Inhibitor

When the above-mentioned corrosion control systems are impractical and/or uneconomical the corrosion control by inhibitor should be implemented.

The chosen corrosion control system should control corrosion effectively and economically with regard to available Engineering Standards.

Selection of inhibitor should be based on knowledge of the production characteristics of the system, field performance tests, and laboratory confirmation of performance.

A partial list of field factors that should be considered in inhibitor selection are listed with brief notes below.

6.10.1.1 Transmission Lines: Gas

Factors affecting inhibitor selection:

- Volume transmitted
- Line pressure, temperatures
- Line sizes and lengths
- Associated liquids (water and condensate)
- Gas and water analyses
- Use of methanol injection for hydrate control
- Field contours
- Location of field dehydrators and fluid residence times
- Inlet separator facilities and retention times
- Presence/absence of asphaltene/iron sulfide/elemental sulfur.

Flow speed in gas transmission lines is a significant factor affecting corrosion. At low flow speeds (usually 3 m/s or less), liquid drop-out, particularly water, can lead to a corrosive situation. Field contours can be critical – valleys followed by steep uphill sections of line lead to liquid accumulation. The area of gas breakout (splash zone) is particularly vulnerable to pitting corrosion, leading to early line features.

Inlet separator size and fluid residence time are of importance in systems where fluid (water and condensate) volumes are significant compared to the gas volumes. If residence times are short, the corrosion inhibitor must not only protect the system, but also provide quick, clean separation of condensate from water.

Recommendations for corrosion inhibition of gas gathering systems should take into account the following:

- Flow regimes and flow speeds in the system
- Selection of inhibitor to meet gas and liquid characteristics and separator factors
- Economy of injection rate with full consideration of surface area protected, and gas and water production levels.

6.10.1.2 Transmission Lines: Oil, Oil and Solution Gas

Factors affecting selection include:

- Volumes transmitted
- Line sizes and lengths
- Gas/oil ratio and gas composition
- Flow regimed
- Water and solution gas analyses.
- Presence/absence of wax/asphaltene/iron sulfide.

Brine levels have considerable significance in the selection of inhibitors. If a field is on water injection, breakthrough to some wells will affect water composition and corrosive properties. In such cases analytical data may be required from a number of wells in the system. Production from different zones may also give rise to different corrosion characteristics and inhibitor distribution ratios between oil and water phases.

6.10.1.3 Storage Tanks and Tankers

Inhibition of storage tanks and tankers handling crude oil and/or petroleum products should be based on consideration of corrosion control by inhibitor.

6.10.1.4 Laboratory Evaluation

Laboratory evaluation of nominated inhibitor(s) should, in addition to the already tests described, include a persistency study, a distribution study, and a stability study of the inhibitor(s), as well as inhibitor film development, and the subsequent resistance of the film to displacement and loss of protective efficiency by medium. Information should be acquired on the amount of inhibitor necessary to provide protection in a system and the most economical rate of addition to ensure protection.

6.11 Biological Control in Oil and Gas Systems

Micro-organisms (bacteria, "bugs") can produce serious effects in oil and gas systems. Bacteria can cause or contribute to:

- corrosion of pipelines and equipment,
- plugging of injection lines, well bores or formation.

Bacteria are frequently classified according to their need for oxygen to grow and multiply. The three categories are:

1. Aerobic bacteria: require oxygen to grow.
2. Anaerobic bacteria: grow in the absence of oxygen.
3. Facultative bacteria: grow in the presence or absence of oxygen.

In an oil or gas system three general types are likely to be encountered:

- *Slime formers*. Aerobic or facultative bacteria that produce dense slimes on solid surfaces can cause plugging and contribute to corrosion by shielding the surfaces from the protective action of corrosion inhibitors.
- *Iron bacteria*. Deposit a sheath of iron oxide around them as they grow. They can cause plugging and create conditions that lead to corrosion.
- *Sulfate-reducing bacteria (SRBs)*. Cause the most serious problems in systems. They can create pitting corrosion directly below a colony of bacteria, produce iron sulphide, leading to plugging, and generate H_2S, leading to an increase in corrosion rates and pitting and/or sulfide cracking throughout a system. Because these bacteria grow in groups or colonies on pipe walls and steel surfaces, pitting occurs wherever they thrive. Furthermore, because they are normally attached to a surface, a positive test on a fluid sample usually indicates a severe infestation of the system.

6.11.1 Culture and Identification

Cultures of samples made in the field using septum culture bottles containing a growing medium can give information on the bacteria present and the degree of contamination.

The culture bottle technique employs successive dilutions of the field water in the culture media. The more dilute the sample bottle that shows bacterial activity, the more contaminated the field water sample. This technique is termed "extinction dilution" or "serial dilution." With suitable culture media bottles this method can be used for either aerobic bacteria or sulphate-reducing bacteria.

As a general guide, for aerobic bacteria, counts of less than 10 000 per ml are not normally considered significant, counts of 50 000–100 000 per ml indicate a strong probability of plugging and requirement for treatment. Any positive identification of sulfate-reducing bacteria indicates a problem.

6.11.2 Scales and Deposits

As bacteria often attach themselves to pipe walls or under scale, culture of deposits or scrapings can frequently detect bacterial contamination, when culture of water samples has provided inconclusive results, but there is field evidence of bacterial problems.

6.11.3 Chemical Control

Chemical control can be classified into four types:

- Bactericides
- Bacteriostats
- Biocides
- Biostats.

In oil and gas operations control of "forms of life," other than bacteria, discussed above, frequently means control of algae. Algae form slime and grow on water surfaces exposed to air, such as holding ponds or disposal pits. Subsequent injection of algae-containing water into disposal wells can cause plugging problems. Algal growth in a pond or pit can also provide a good environment for bacterial growth.

Chemicals available for bacterial and/or algal control may be inorganic or organic. Chlorine (inorganic) is widely used for biocidal control, either injected as gas or generated in the system from bleach (sodium hypochlorite solution – usually supplied as a 12% available-chlorine solution).

A wide range of organic formulations are available. The general classes are amines, quaternary ammonium compounds, and aldehydes. Some specific compounds that have in recent years been found to be particularly effective against oil-field bacteria are isothiazolones and halogenated amides. Consideration in the selection of a chemical control system should be as follows.

6.11.3.1 Complete Kill or Control?

Sulfate-reducers require a bacteriocide to obtain a total kill. A moderate number of aerobic species (bacterial or algal slime formers) can be tolerated without serious problems, thus a bacteriostat or biostat may be sufficient for control.

6.11.3.2 Source of Biological Species and Control Points

It is important to determine the source of the biological problem. For example, gas-producing systems are normally free of biological activity. Contamination can arise from the introduction of bacteria with well-workover or completion fluids. Once established, such down-hole bacteria can continue to give problems.

Treatment at the down-hole source may be required and the formulation chosen should be effective and not cause production problems such as emulsion blocks following treatment.

In oil systems, biological control may require batch treatment to kill established growth, as well as continuous treatment of water-disposal systems.

Injection points should be selected to avoid interference problems with other chemicals in the system.

6.11.3.3 Economics

Chemical control should be selected on a cost-effective basis. The cost per liter of a formulation is less important than the total cost of achieving biological control when a selection is made. If continuous injection is required, an initially high dosage is recommended followed by a lower maintenance

dosage. The cost should then be considered on an ongoing basis over a period of several months or a year.

6.11.3.4 Method of Application

Chemical control agents can be applied as batch treatments, at high concentrations injected over a short period, or continuously. The method should be selected according to the characteristics of the system and the sources and degree of contamination. Addition rates should be adjusted from monitoring the performance in the system.

6.11.3.5 Resistance Time

Some formulations used on a batch basis for control of sulfate-reducers require an adequate contact time for complete kill. If the residence time of water carrying the biocide slug in a vessel is short, full kill may not be achieved. In such cases, injection using a chemical pump over a longer period may be required. On a cost-effective basis, 6 hours per week injection at high concentration may achieve a better kill compared to continuous injection at a low rate, 24 hours per day.

In selection, tests made by consulting laboratories of kill versus time should take into account the performance of a formulation over a period of time, as some formulations take 48–72 hours to establish full control.

6.11.3.6 Monitoring

A biological control program should include regular monitoring of field samples. Use of biological control products should be supported with field monitoring programs. Injection rate adjustments should be performed on the basis of data obtained from field tests.

6.11.3.7 Interferences

Performance of biological control formulations in the system can be affected by other chemical control programs (e.g. oxygen scavengers, some corrosion inhibitors). Oxygen scavengers and biocide formulations are usually incompatible. Widely separated injection points are advisable.

Hydrogen sulfide can also react with some formulations, resulting in decreased activity. The manufacturer's technical service group should be consulted on selection of products for water containing H_2S and biological contamination.

6.11.3.8 Resistance

Bacteria may, over time, develop strains resistant to a particular formulation. Change of biological control formulation at intervals is advisable, particularly if the treatment method is continuous at low addition levels.

Proper diagnosis of a field biological problem and its control is frequently a complex process. The assistance of inhibitor suppliers regarding information, details of laboratory evaluations, and recommendations should usually be requested.

6.12 Scale Control in Oil Systems

6.12.1 The Formation of Scale

Water has a tendency to dissolve everything it contacts. Some materials have the limit of their solubility set, primarily, by the temperature of the water and the concentration of other materials

Table 6.2 *Solubilities of some chemical compounds*

	Solubility (mg/L)
$CaSO_4$ (gypsum) dissolved in water → $Ca^{2+} + SO_4{}^{2-}$	2080
$BaCl_2$ (barium chloride) dissolved in water → $Ba^{2+} + 2Cl^-$	320 000
$Ba^{2+} + SO_4{}^{2-} \rightarrow BaSO_4$(barium sulfate)	2.3

dissolved in the water. Most materials that dissolve in water will ionize, that is, break down into ions and/or radicals. These ions may react with other ions such that the resulting material has lower solubility than either of the original materials that were dissolved in the water (for an example see Table 6.2).

Bringing together barium ions (Ba^{2+}) and sulfate ions ($SO_4{}^{2-}$) results in the formation of barium sulphate, which has an extremely low solubility in water. The barium sulfate, consequently, precipitates from the water as crystals that we call scale.

The precipitation of solid material that may form scale will occur when the temperature, composition, and pressure of the water changes to produce a solubility limit that is lower than the present concentration of the solid, and when ions react with one another to form a new material that has a lower solubility than the ions in solution.

Solids that separate from water may do so as small crystals and deposit in a crevice, in a collar, or even between grains of sand in a producing formation. The small crystals may grow in size as more of the same material comes out of solution until it is recognized as a scale by covering a large surface area. The solids may separate from water without forming a scale, as microcrystalline particles, resulting in a sludge or turbidity in the water. This turbidity may settle and form a starting place for scale of another chemical type. For instance, a sludge of calcium sulfate and sand may be covered over or cemented together with calcium carbonate. This is the usual manner of formation of oil-field scales.

Scale frequently deposits in the oil formation near the well bore, in the perforations, or even on the face of the formation. Scale can form over the inlet ports of a rod pump or a Reda pump, starving them of fluid and possibly causing the Reda to get hot and burn out. Scale can form in the pump itself, even though the velocity of fluid movement is high. Fire tubes in all types of heaters fail prematurely when scale formation results in overheating. Corrosion is often more severe under a scale deposit.

Because of these problems, scale control should be of primary concern in the production of oil and the injection of water.

6.12.2 Oilfield Scales

6.12.2.1 Calcium Carbonate

Calcium carbonate is a slightly soluble salt occurring in nature in the form of minerals such as calcite, limestone, dolomite, and marble. The solubility is much greater in acids. Carbon dioxide in the air or within oil formations dissolves in water to form carbonic acid, H_2CO_3. This acid converts the carbonates in calcium carbonate to soluble bicarbonates that can be dissolved in water.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{6.3}$$

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3{}^- \tag{6.4}$$

$$CO_2 + H_2O + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3{}^- \tag{6.5}$$

The amount of CO_2 that will dissolve in water is proportional to the amount of CO_2 in the gas over the water and the pressure of the system. So, if either the system pressure or the percentage of CO_2 in the gas were to increase, the amount of CO_2 dissolved in the water would also increase, allowing more calcium carbonate to be dissolved.

The reverse is also true, and is one of the major causes of $CaCO_3$ scale deposition. At any point in the system where a pressure drop is taken, CO_2 comes out of solution, and the pH of the water rises. This shifts reaction (6.3) to the left and may cause $CaCO_3$ precipitation. If the pH is lowered by the use of any acid, the solubility of calcium carbonate is increased; the acid does not have to be carbonic acid from the solution of carbon dioxide in water. Any increase in alkalinity, on the other hand, increases the tendency to form a precipitate.

Contrary to the behavior of most materials, calcium carbonate becomes less soluble as the temperature increases: the hotter the water gets, the more likely $CaCO_3$ scale will form.

Water that cools as it flows up to the tubing will not deposit carbonate because of temperature change, although loss of CO_2 from the water can be of concern. The same water in contact with a heater tube may deposit scale readily on the fire tube. The increase of temperature in water injection wells can result in carbonate scale deposition.

Calcium carbonate solubility increases with the salt content of the water. The higher the total dissolved solids (not counting calcium or carbonate), the greater the solubility of $CaCO_3$ in the water.

The tendency for calcium carbonate scale to form increases as:

- temperature increases
- pH increases
- pressure drops
- water with high salts content is diluted.

6.12.2.2 Calcium Sulfate

Most calcium sulfate scales in oil-field work are gypsum, which has the formula $CaSO_4.2H_2O$. The solubility of gypsum is greatest at 43 °C. A temperature change can make either an increase or a decrease in solubility depending on its position on the curve.

Calcium sulfate may also be deposited as anhydrite ($CaSO_4$) at temperatures above approximately 43 °C. Note from Figure 3/2 that the solubility of anhydrite is less than that of gypsum above that temperature. It can be expected that anhydrite might be the preferred form of $CaSO_4$ in deeper, hotter wells.

Dissolved salts, other than calcium or sulfate ions, increase the solubility of gypsum or anhydrite up to a salt concentration of about 150 000 mg/L. Further increases in salt content decrease $CaSO_4$ solubility. Solubility is three times greater in brine containing 150 000 ppm of salt than in distilled water. The effect of pressure is small.

6.12.2.3 Barium and Strontium Sulfates

Barium sulfate and strontium sulfate are similar, often found together and often reported as barium. The very low solubility of each makes the formation of a precipitate certain if a water containing either barium or strontium ions is mixed with one containing sulfate (SO_4^{2-}) ions.

Barium sulfate solubility increases with temperature and because of this, barium sulfate usually presents no down-hole scaling problems in an injection well if it is non-scaling at surface conditions. It is more commonly a problem in producing or source wells.

The solubility of barium sulfate in water is increased by dissolved salts, just as for calcium carbonate and calcium sulfate. There is a 13-fold increase brought about by the addition of 100 000 mg/L NaCl with no change in temperature.

6.12.2.4 Iron Compounds

Iron in water may be either naturally present or the result of corrosion. Formation waters normally contain only a few mg/L of natural iron; values up to 50 ppm are possible. Higher values are from corrosion.

Carbon dioxide will react with iron to form iron carbonate. Scale is likely to form if the pH is above 7. Hydrogen sulfide will form iron sulphide, which will form a thin scale, or will be suspended as small particles to give "black water."

Oxygen will form various compounds with iron that are generally reddish. They often become trapped in the matrix of other scale deposits, giving a reddish color to the normally brown or gray scales.

6.12.2.5 Miscellaneous

There are some deposits that are not scale, but are related: the sludges. Some sludges consist of considerable organic matter such as wax, asphaltenes, or tar. The deposits may be hard and crumbly, or soft and mushy.

Sand, silt, and drilling mud are often incorporated as parts of a scale, or are laid down as hard deposits that are called "scale." Corrosion products, as discussed above, are not true scales but, again, are solid products that are often called "scales."

6.12.3 Preventing Scale Formation

6.12.3.1 Avoid Incompatible Water

One of the primary causes of scale formation is mixing two or more waters that are incompatible. The separate waters may be stable, but react to form a precipitate when mixed.

Mixing water produced from an oil well with water from a lake, river, or source well must be checked. Likewise, mixing a proposed injection water with the natural formation water must be evaluated.

The tendency for waters to form a precipitate when mixed can be evaluated by calculation, as discussed later, or by mixing the waters in a clear bottle, then setting aside for several days for observation.

6.12.3.2 Modify the Water

Water may be modified so that a precipitate of scale will not be formed by:

- removing the scale-forming components
- lowering the pH
- blending with another water.

In practice, none of these methods find much use – primarily because of cost.

Dissolved gases such as H_2S, CO_2, and O_2 can be removed from the water. This will eliminate iron sulfide and the various iron dioxides, all of which from insoluble compounds. Removing CO_2 however, will increase calcium carbonate deposition.

Lowering pH reduces scale-forming tendency, but increases corrosion. It is practical only for small volumes of water such as boiler feed water or cooling systems.

Blending several waters must be handled with care, as discussed previously. Either diluting scale-forming components or increasing the salt concentration could be helpful.

6.12.3.3 Scale-Control Chemicals

The formation of crystals from a liquid solution is thought to develop as follows:

1. Micro-crystalline particles form throughout the liquid. The crystals are extremely small, and are all similar in size and structure. The number of crystals depends primarily on temperature and concentration. This step is termed nucleation, since the small crystals are nuclei upon which the larger crystals develop.
2. The crystals grow by adsorbing ions from solution onto the surface of the crystal.
3. As the size of the original particles increases they become joined together in a process called coagulation.
4. Finally, there is competitive growth in which the larger particles grow at the expense of the smaller, which go into solution.

Scaling and deposition of crystalline chemical compounds can be controlled in several ways:

1. An impurity can be introduced into the crystals as they form that either blocks further growth or introduces strain into the crystalline structure.
2. Ions can be added that are adsorbed on the surface of the crystal, slowing and otherwise interfering with its further growth.
3. Chemicals can be added that form soluble compounds with the scale- .
4. The surfaces upon which the scale would deposit are made "slick."

The concentration of scale inhibitor required depends upon the temperature, the composition of the salt that precipitates, and the salt concentration. The higher the salt concentration and temperature, the greater the concentration of inhibitor needed to successfully prevent precipitation. The effectiveness of the inhibitor depends upon the tenacity of the chemisorption bond it forms with the surface of the particle.

Methods of scale control are: sequestration or chelation, film formation, or nucleation. A particular scale inhibitor may act as both a sequestration and a nucleation agent.

Sequestering chemicals react with certain scale-forming constituents to form new compounds that are still soluble, but which are unreactive. A well-known example of this type of material is sodium hexametaphosphate, a water-softening agent that ionizes in water to furnish the hexametaphosphate ion. This then reacts with "polyvalent" ions such as calcium and magnesium. The resulting calcium or magnesium hexametaphosphate is water soluble, but does not reionize. The end result is to completely tie up the calcium and magnesium ions in a water-soluble, unreactive form, thus preventing them from precipitating as calcium carbonate or magnesium hydroxide, typical scale-forming compounds.

Chelating agents are a special class of sequestering chemicals. They tie up the ions in non-ionizing forms, as do all the sequesterial agents, but they are distinctive because this is done in a very special way: the chelating agents employ a special type of chemical bonding to isolate the offending ions. Chelate-type chemical bonds are unusually strong. Most chelating agents for scale control lose efficiency as pH drops, so it is customary to formulate such materials with alkaline chemicals that will raise the pH of the system.

The film-formers operate through their ability to lay down thin, adherent, organic films on solid surfaces. They are usually semipolar compounds having a large, strongly polar group at one end and an oil-soluble tail at the other end. Generally accepted theory is that the polar end of the molecule is electromagnetically attracted to the solid surface, while the hydrocarbon "tail" stands out from the solid surface. Theory further concludes that the filming molecules pack closely together on the surface with their hydrocarbon tails "oriented" in one direction like the hairs in a horse's coat.

Many chemists and engineers believe that, in order to have a good protective film, one must have a third component in addition to the polar "heads" attached to the surface and the "coat of hydrocarbon tails." The third component is a film of oil attracted to the hydrocarbon tails. This theory gains support from the fact that some of the semipolar film formers are not effective in 100% aqueous systems, where there is no oil available to form a film over the hydrocarbon "tails."

A second view is that films deposited on the pipe walls prevent "seeding" or "nucleation" of the depositing salts. Crystals such as those in scales need sharp edges and angles to start forming. In supersaturated solutions, it is possible to "seed-out" or "nucleate" the salts by introducing crystals of the same salts or by scratching the surface of the container to provide sharp edges and angles on which the crystals may form. Any agent that coats the container walls with a smooth film will decrease the tendency to form crystals.

Support is given to this theory regarding the mechanism of action of film formers by the fact that plastic pipe or plastic-coated pipe occasionally is scale-free.

The operation of nucleating chemicals is not perfectly understood. The consensus is that they work by furnishing many millions of tiny nuclei or seeding-centers that create a tremendous total surface area on which scale-forming salts will deposit preferentially. Since there are so many of these nuclei, none of them receives a large amount of depositing salts. As a result, the system contains huge numbers of very minute scale particles rather than smaller numbers of large particles. The smaller particles have a much greater tendency to be carried in the main body of the flowing fluid and are not as likely to contact the pipe walls as the large particles.

An alternative viewpoint as to the mechanism by which nucleating agents work renders the distinction between "nucleating agents" and "film-formers" less clear. The contention is that the chemicals act through adsorption on the salt crystals as they first form. The adsorbed film on each of the crystals prevents further crystal growth and the end result is that the system contains many millions of very minute crystals.

6.12.4 Relative Effectiveness of Scale Control Chemicals

Nucleating agents can perform very well at unbelievably low dosages. This has been established by the fact that polyphosphates (which are also sequestering agents) perform at dosages that are only a very small fraction of those theoretically required to sequester the salts known to be present. This remarkable increase in effectiveness is attributed to nucleation.

Scale control chemicals that act as nucleating agents frequently are the only chemicals that can be economically justified for use in oil wells producing large volumes of water and heavy scale deposits.

Although they are not generally as reliable as the polyphosphate-type, organic filming agents frequently are able to do quite a good job at low dosages. So long as there is enough oil in the system to insure that they have adequate contact with the metal surfaces to be protected.

Their dosage requirements are virtually independent of the total amount of scale-depositing salts present. Presumably this is because a large amount of the film-forming agent can be consumed in coating the very surface areas presented by a relatively small amount of minute scale crystals.

Film-forming thus can be economically attractive for use in high-water-volume oil wells, but dosage requirements may become excessive in such wells if the scale problems are severe; that is, if very large amounts of scale-forming constituents are present.

Because they involve direct chemical reaction, the sequestering agents or chelating agents can do exceptionally complete jobs in inhibiting scale formation. However, dosage requirements become prohibitive in systems where a large excess of scale-forming constituents is present. This occurs because the sequestering or chelating agents tie up only one or two molecules of scale-forming salt per molecule of sequestering agent.

Generally the commonly used, less-expensive sequestering agents for oil wells are water-soluble. This is necessary because the ions they must tie up are in the water phase. However, this situation means that an extremely large amount of sequestrate must be added to an oil well producing large

water volumes, in order to produce a reasonable concentration in the water phase. Thus, the sequestering agents or chelating agents can usually only be justified economically for use in wells producing small or moderate water volumes and containing only small to moderate amounts of scale-forming constituents.

6.12.5 Types of Scale Inhibitor

The common inhibitors for scale control in water systems include:

- Organophosphonate general purpose scale inhibitor. Suitable for situations where calcium carbonate is the principal component of scale formed.
- Calcium carbonate scale inhibitor.
- Calcium sulfate scale inhibitor.
- Gyp-scale converter/remover.
- Acrylate scale inhibitors for water flood applications.
- Corrosion/scale inhibitor for water disposal systems.
- Phosphonate scale inhibitor for sulfate scale situations. It prevents formation of calcium, strontium and barium sulfate scale, as well as calcium carbonate.
- Phosphonate scale inhibitor, which should be particularly designated for steam flood and other high temperature applications. It may be squeezed into the formation.
- Organic amine phosphate formulations. Suitable for producing wells with severe down-hole scale problems. It should be formulated in a hydrocarbon carrier solvent system.
- Corrosion inhibitors formulated with scale control components.
- Acrylate-type scale inhibitors for injection systems. Scale removers.

6.12.6 Identification of Scale

There are times when the engineer in the field is called upon to identify scale samples. An operator may need to take immediate steps to remove scale from production tubing, flow lines, or other pieces of equipment, and time does not permit submitting a sample of the scale to a laboratory for analysis. The engineer must be able to determine whether the scale is calcium carbonate, iron carbonate, calcium sulfate, barium sulfate, or a combination of scales. The following procedures outline various methods that the field engineer may use to determine the type of scale in question.

Prior to subjecting any scale sample to an analytical procedure, the sample should be rinsed in a suitable solution of water and a surfactant to water-wet any preferentially oil-wet sample.

6.12.6.1 Step I

Place a sample of the scale in a beaker and add enough 15% or 37% hydrochloric acid to cover the scale sample. If there is a rapid effervescence (bubbling effect) and the sample dissolves, the scale is calcium carbonate ($CaCO_3$). If the effervescence is very slow, heat the acid to approximately 65.5 °C (150 °F). If the rate of effervescence increases with the addition of heat, and the acid solution turns yellow, the scale is iron carbonate ($FeCO_3$).

If a reaction does not take place in the hydrochloric acid solution, proceed to Step II.

6.12.6.2 Step II

Place a sample of the scale in a beaker and add enough caustic soda solution (25% by weight) to cover the scale sample. If the sample disintegrates and forms a slurry in the bottom of the breaker, the scale is calcium sulfate ($CaSO_4$).

If a reaction does not take place, proceed to Step III.

6.12.6.3 Step III

If the sample is dark brown or black in color, the scale could possibly be iron sulfide or magnetite. Place a magnet into a crushed sample. If the magnet picks up a major portion of the sample, the scale is magnetite. If there is no attraction to the magnet, place a few drops of Iron Sulfide Detecting Solution on the sample. If a bright yellow precipitate is formed, the scale is iron sulfide.

If both test results are negative, proceed to Step IV.

6.12.6.4 Step IV

Wash the sample in a solvent (benzene, oxylene, etc.) to remove all hydrocarbons. Rinse the sample in distilled water to remove salt crystals. Crush the sample and mix with enough 37% hydrochloric acid to form a slurry. Dip a platinum wire into the slurry and insert the wire into the flame of a Bunsen burner. Note the color of the flame: calcium will emit an orange flame of short duration; barium will emit a green flame of relatively long duration; strontium will emit a crimson flame of relatively long duration.

6.12.7 Predicting Scale Formation by Calculation

The values obtained from these calculation procedures should be taken only as guidelines. They indicate the likelihood of scale formation. Many assumptions had to be made in developing the method of calculation, which may not apply to the specific water being evaluated. If scale formation is indicated by calculation, it serves as an alarm. If you are looking at a possible water source, you should avoid those that show scaling tendencies or make provision for treatment. Similarly, you should avoid mixing waters where the blend exhibits scaling tendencies under system conditions.

Some of the critical properties of water change very quickly after sampling. These properties should be determined in the field immediately after the sample is taken in order to determine an acceptable scaling tendency. Two properties that should be determined in this manner to have any value are pH and bicarbonate (HCO_3^-). The instant that the pressure is reduced, any dissolved "acid gases" (H_2S and CO_2) will begin to escape from the water and the pH will begin to rise. The loss of dissolved CO_2 will have a direct effect on the bicarbonate and carbonate concentrations. Generally only bicarbonate determination is needed; carbonate concentration is small.

6.12.7.1 Calcium Carbonate

Calcium carbonate precipitation is caused by a shift toward carbonates in the carbonate–bicarbonate–carbon-dioxide equilibrium. When the equilibrium shifts in the other direction, the precipitate goes back into solution. Since there is usually considerable delay between the establishment of an equilibrium and the precipitation or dissolution of calcium carbonate, unstable conditions exist in which water will precipitate or dissolve calcium carbonate on standing.

Langelier developed an equation setting forth the conditions of the carbonate equilibrium. By the use of this equation, the pH of water at equilibrium can be calculated. If the pH is higher than the calculated pH, the water has a tendency to form scale; if it is lower, the water has a tendency to be corrosive. Langelier's equation can be expressed in a single form as follows:

$$SI = pH - pCa - pAlk - K \tag{6.6}$$

where:

- SI is the stability index. A positive index indicates scale formation. A negative index indicates corrosion. This equation was derived with many assumptions that do not apply in all cases. Because of this, the results should not be applied too adamantly. If SI is +0.5 or above, consider the system

as having a tendency to scale. Any value between 0.5 and 2.5 will indicate a probable scaling problem; the higher the value, the more likely the formation of scale.

- pH is the pH of the water sample as actually determined. The value must be determined in the field immediately after the sample is taken, to be reliable. The pH value should be recorded on the bottle label or on the Lab Request Sheet.
- pCa is the negative logarithm of the calcium concentration.

$$\mathrm{pCa} = 8.922[\mathrm{Ca}^{2+}]^{-0.2708} \tag{6.7}$$

- pAlk is the negative logarithm of the total alkalinity. Bicarbonate $(\mathrm{HCO}_3)^-$ must be determined in the field, and handled in the same manner as pH. If bicarbonate and pH are not determined accurately on the fresh water sample, the calculated SI loses most of its value.

$$\mathrm{pAlk} = 8.1997[\mathrm{HCO}_{3^-} + \mathrm{CO}_3{}^-]^{-0.23638} \tag{6.8}$$

- K is a constant, the value of which depends on the total salt concentration and the temperature.

In this section, a novel and simple predictive tool is presented to estimate the formation of calcium carbonate scaling as a function of pH, temperature, ionic strength of the solution, calcium cation concentration, bicarbonate anion concentration, and carbon dioxide mole fraction when the water mixture is saturated with a gas containing CO_2, to evaluate the effect of solution conditions on the tendency and extent of the precipitation. The proposed method covers calcium cation concentrations, or bicarbonate anion concentrations up to 10 000 mg/L, temperatures up to 90 °C, total ionic strength up to 3.6, and pH values ranging between 5.5 and 8.

pH, $[\mathrm{Ca}^{2+}]$, and alkalinity content of the water are variables that control the calcium carbonate saturation equilibrium value at the temperature of the water. The process of fouling in the water is very complicated, consisting of four steps: (1) ions in water form salt molecules with low solubility; (2) molecules bond and arrange to form minicrystals, and begin to granulate; (3) lots of crystals congregate, deposit, and cause fouling; (4) various types of scale are formed in different conditions.

Due to the complexity of the precipitation process, the saturation index (SI) is calculated to estimate the calcium carbonate precipitation in water, and is used to describe the saturation state (from a thermodynamic point of view) of the aqueous phase composition versus different solids. It is widely used to estimate the potential precipitation of different solids from an equilibrated aqueous phase speciation.

When the SI is equal to zero, the solution is in equilibrium; when negative, the solution is undersaturated and no precipitation occurs; when positive, the solution is supersaturated and precipitation could occur. Therefore, SI values can be used as a guide to evaluate the effect of the solution conditions on the tendency and extent of precipitation. Calcium carbonate dissolution is a mass-transfer-limited process at room temperature, and therefore calcium carbonate dissolution occurs quickly relative to the other processes operating in the system.

The chemistry of calcium carbonate deposition can be understood by examining the following formulae:

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{H}_2\mathrm{CO}_3 \tag{6.9}$$

$$\mathrm{H}_2\mathrm{CO}_3 + \mathrm{CaCO}_3 \leftrightarrow \mathrm{Ca}^{2+} + 2\mathrm{HCO}_3{}^- \tag{6.10}$$

So overall reaction will be:

$$\mathrm{HCO}_3{}^- + \mathrm{OH}^- \rightarrow \mathrm{CO}_3{}^{2-} + \mathrm{H}_2\mathrm{O} \tag{6.11}$$

$$\mathrm{CO}_3{}^{2-} + \mathrm{Ca}^{2+} \rightarrow \mathrm{CaCO}_3{}^{2-} \downarrow \tag{6.12}$$

As pressure decreases during production, CO_2 is released and $CaCO_3$ precipitates:

$$Ca(HCO_3)_2 \rightarrow CO_2 \uparrow + H_2O + CaCO_3 \downarrow \tag{6.13}$$

Deposition of calcium carbonate will occur if the reactions are shifted to the right. The following may cause this shift:

- Increase in temperature
- Decrease in pressure
- Loss of dissolved carbon dioxide
- Increase in pH.

Langelier was the first scientist to develop the scale prediction formula:

$$pH_s = pCa - pAlk - K \tag{6.14}$$

Stiff and Davis have simplified the work of Langelier on the scaling index of oil-field waters, i.e. their tendency to deposit calcium carbonate scale. They defined the stability index (SI) as follows:

$$SI = pH - pCa - pAlk - K \tag{6.15}$$

$$SI = pH - pH_s \tag{6.16}$$

The saturation index (SI), is widely used as a qualitative indication of the amount of potential $CaCO_3$ deposition. In light of the above-mentioned status, currently there is an essential need for the development of a practical, reliable and easy-to-use predictive tool for practice engineers and researchers for the accurate determination of pH required to precipitate $CaCO_3$. This section therefore discusses the formulation of a simple predictive tool that can be of significant importance for engineers.

Equation (6.17) represents the proposed governing equation in which four coefficients are used to correlate the correction factor (K) as a function of temperature and total ionic strength where the relevant coefficients are given in Table 6.3.

$$\ln(K) = a + bI + cI^2 + dI^3 \tag{6.17}$$

where:

$$a = A_1 + \frac{B_1}{T} + \frac{C_1}{T^2} + \frac{D_1}{T^3} \tag{6.18}$$

$$b = A_2 + \frac{B_2}{T} + \frac{C_2}{T^2} + \frac{D_2}{T^3} \tag{6.19}$$

$$c = A_3 + \frac{B_3}{T} + \frac{C_3}{T^2} + \frac{D_3}{T^3} \tag{6.20}$$

$$d = A_4 + \frac{B_4}{T} + \frac{C_4}{T^2} + \frac{D_4}{T^3} \tag{6.21}$$

These optimum tuned coefficients help to predict the correction factor (K) as a function of total ionic strength for temperatures up 90 °C, as well as total ionic strengths up to 3.6. The optimum tuned coefficients can be retuned quickly according to the proposed approach if more data are available in future.

Figure 6.1 can be used as an alternative method to calculate K.

The above-mentioned methodology is applied to correlate the solubility factor (S_f) as a function of temperature and pressure and Equations 6.22–6.26 are the results of this modeling. Table 6.5 provides coefficients for Equation 6.22.

$$\ln(S_f) = a + bT + cT^2 + dT^3 \tag{6.22}$$

Table 6.3 *Tuned coefficients used in equations to calculate K correction factor*

Coefficient	Values for T < 50 °C	Values for T > 50 °C
A_1	$-4.01872209084 \times 10^{1}$	$-2.391149881792 \times 10^{1}$
B_1	$3.358632412104 \times 10^{4}$	$1.8829775434 \times 10^{4}$
C_1	$-9.332090424253 \times 10^{6}$	$-4.8999909008 \times 10^{6}$
D_1	$8.830395116243 \times 10^{8}$	$4.42686988727 \times 10^{8}$
A_2	$2.447151172913 \times 10^{1}$	$-6.453426601397 \times 10^{2}$
B_2	$-2.2087984632578 \times 10^{4}$	$6.487483833707 \times 10^{5}$
C_2	$7.00026860892 \times 10^{6}$	$-2.172600587489 \times 10^{8}$
D_2	$-7.516802198485 \times 10^{8}$	$2.426834762552 \times 10^{10}$
A_3	$-2.549534944987 \times 10^{1}$	$4.447440043399 \times 10^{2}$
B_3	$2.317382603188 \times 10^{4}$	$-4.468699413537 \times 10^{5}$
C_3	$-7.183812773571 \times 10^{6}$	$1.496741852598 \times 10^{8}$
D_3	$7.472781676899 \times 10^{8}$	$-1.67250136262 \times 10^{10}$
A_4	5.85541409682	$-8.95515489082 \times 10^{1}$
B_4	$-5.36359226963 \times 10^{3}$	$8.96408340664 \times 10^{4}$
C_4	$1.656955334201 \times 10^{6}$	$-2.99262724741 \times 10^{7}$
D_4	$-1.709904839216 \times 10^{8}$	$3.333749109029 \times 10^{9}$

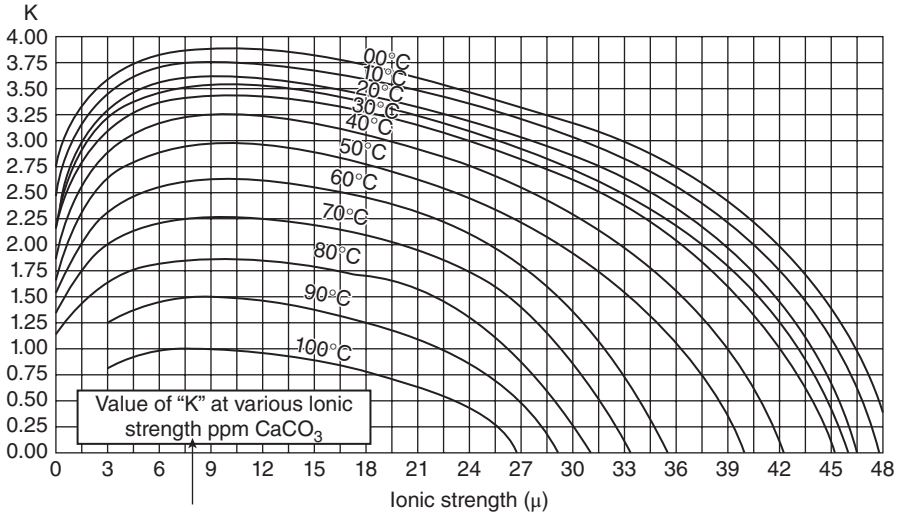


Figure 6.1 *Values of K at various ionic strengths. (Reproduced with permission from Daubert Cromwell.)*

where:

$$a = A_1 + \frac{B_1}{P} \tag{6.23}$$

$$b = A_2 + \frac{B_2}{P} \tag{6.24}$$

$$c = A_3 + \frac{B_3}{P} \tag{6.25}$$

$$d = A_4 + \frac{B_4}{P} \tag{6.26}$$

Then R′ is calculated to take into account the solubility factor, the CO_2 mole fraction and the solubility factor:

$$R' = \frac{C_{HCO_3^-} \times 0.82}{x_{CO_2} \times S_f} \tag{6.27}$$

where:

A, B, C, D = tuned coefficients
I = total ionic strength
K = correction factor for total ionic strength and temperature
pH = actual pH value of the system
pH_s = pH value when the calcium carbonate achieves saturation in the system
S_f = solubility factor
T = temperature, K
P = pressure, kPa
x_{CO_2} = CO_2 mole fraction in water mixture saturated with gas containing CO_2.

Equation (6.28) calculates the pH of the solution.

$$pH = (0.4341)\ln(R') + 6.2964 \tag{6.28}$$

Then Equations (6.29) and (6.30) give pCa and pAlk as functions of $[Ca^{2+}]$ and $[HCO_3^- + CO_3^-]$, respectively.

$$pCa = 8.922[Ca^{2+}]^{-0.2708} \tag{6.29}$$

$$pAlk = 8.1997[HCO_3^- + CO_3^-]^{-0.23638} \tag{6.30}$$

Figure 6.2 can be used for converting parts per million of calcium and alkanity to pCa and pAlk. The following steps are followed in the case of $CaCO_3$:

- Determine the ionic strengths
- Determine *K valu*.
- Determine pCa
- Determine pAlk
- Calculate pHs
- Calculate solubility factor (Sf)
- Calculate R′ ratio.
- Determine pH
- Calculate saturation index (SI).

The proposed simple method covers concentration for calcium cation concentration, or bicarbonate anion concentration up to 10 000 mg/L, temperature up to 90 °C, pressure up to 500 kpa, total ionic strength up to 3.6 and pH between 5.5 and 8.

6.12.7.2 Sample Calculation

On assuming a mixture of 50 vol% seawater and 50 vol% produced water, determine the saturation index (SI) for $CaCO_3$. Assume that the water mixture is saturated with gas containing 5 mol% CO_2 at 1 bar total pressure. Table 6.6 shows the water analysis for this example calculation.

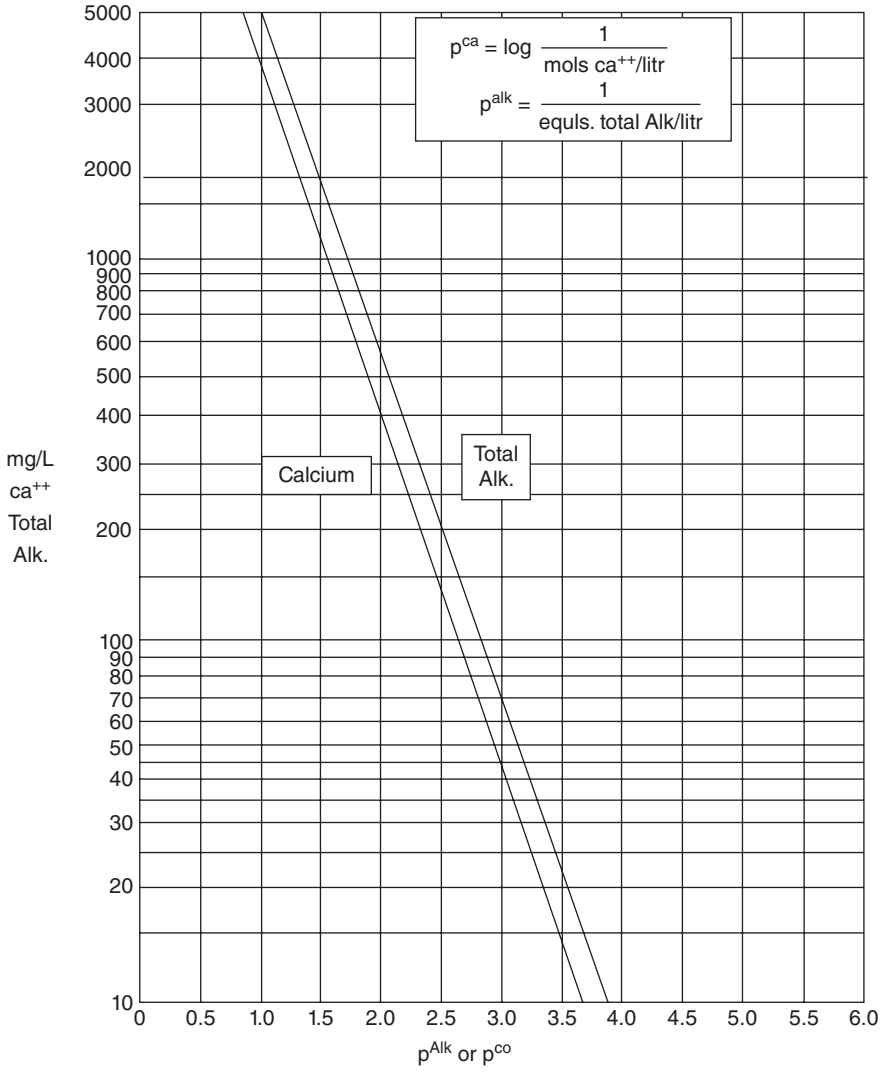


Figure 6.2 *Graph for converting parts per million of calcium and alkalinity into pCa and pAlk. (Reproduced with permission from Daubert Cromwell.)*

The following steps are followed:

- Determine the ionic strengths using Table 6.4:

$$Na^{+} : 0.431$$

$$Ca^{2+} : 0.361$$

$$Mg^{2+} : 0.156$$

$$Cl^{-} : 0.6722$$

$$SO_4^{2-} : 0.031$$

$$HCO_3^{-} : 0.002$$

Thus, the total ionic strength (sum of the above) is equal to 1.653.

$$a = 0.43273776024$$

$$b = 0.80806590964$$

$$c = -0.374183375691$$

$$d = 0.04588308132$$

$$K = 2.5942242138$$

$$[Ca^{2+}] = 7237 \text{ mg/L}$$

$$[HCO_3^{-}] = 325.5 \text{ mg/L}$$

- Determine pCa = 0.80406
- Determine pAlk = 2.0887
  Thus

$$pHs = K + pCa + pAlk = 5.487$$

- Determine ratio R′ (assuming that the gas in contact with water contains 5 mol% CO_2 at a total pressure of 1 bar):

$$R' = \frac{(\text{mg/L}\,HCO_3^-) \times 0.82}{(\text{mole fraction } CO_2) \times S_f} = \frac{325.5 \times 0.82}{0.05 \times 40} = 133.4$$

where the mole fraction of CO_2 is determined from gas analysis and S_f is the solubility factor determined at a temperature of 60 °C (333.15 K) and a pressure of 100 kPa.

$$a = -1.2258068272 \times 10^2$$

$$b = 1.29813880169$$

$$c = -4.16048659204 \times 10^{-3}$$

$$d = 4.20818900382 \times 10^{-6}$$

$$S_f = 41.602$$

Table 6.4 *Factors for converting ion concentration (mg/L or meq/L) to ionic strength, Concentrations must be multiplied by the factors shown*

Ion	mg/L	meq/L
Na^+	2.2×10^{-5}	5×10^{-4}
Ca^{2+}	5×10^{-5}	1×10^{-3}
Mg^{2+}	8.2×10^{-5}	1×10^{-3}
Cl^-	1.4×10^{-5}	5×10^{-4}
SO_4^{2-}	2.1×10^{-5}	1×10^{-3}
HCO_3^-	0.8×10^{-5}	5×10^{-4}

Table 6.5 *Tuned coefficients used in equations for solubility factor (S_f) calculations*

Coefficient	Value
A_1	4.92810471447
B_1	$-1.275087874435 \times 10^4$
A_2	$4.513600203525 \times 10^{-2}$
B_2	$1.253002799657 \times 10^2$
A_3	$-1.078155499373 \times 10^{-4}$
B_3	$-4.052671042103 \times 10^{-1}$

Table 6.6 *Water analysis used for sample calculations in example*

	Seawater		Produced water	
Ion	mg/L	meq/L	mg/L	meq/L
Na^+	11144	484.5	28543	1241
Ca^{2+}	464	23.2	14010	700.5
Mg^{2+}	1350	111	2470	202.5
Cl^-	19900	562.1	75500	2126.8
$SO_4{}^{2-}$	2600	54.1	432	9
$HCO_3{}^-$	149	2.5	502	8.2
TDS	35607	–	121457	–
Sp. Gr.	1.026	–	1.088	–
pH	7.8	–	7.4	–
O_2	3.8	–	–	–
H_2S	0	–	190	–

- Determine pH (pH versus R′):

$$\mathrm{pH} = 8.4206$$

pH decreases with increasing concentration of CO_2 in water.

- Determine saturation index (SI):

$$\mathrm{SI} = \mathrm{pH}(\textit{actual}) - \mathrm{pH_s}$$

$$\mathrm{SI} = 8.4206 - 5.487 = 2.933$$

If the saturation index (SI) is positive, $CaCO_3$ scale formation is likely to occur in the water system. This is a classic example showing how the information evolving from this predictive tool can be used to understand and estimate the saturation index issues that could potentially influence the formation of scale in water.

6.12.7.3 Barium Sulfate

Because $BaSO_4$ has such limited solubility, the appearance of Ba^{2+} and $SO_4{}^{2-}$ ions in any water indicates a strong possibility of scale formation. Data from Templeton, giving the solubility of barium sulfate in brine at various temperatures is given in Figure 6.3.

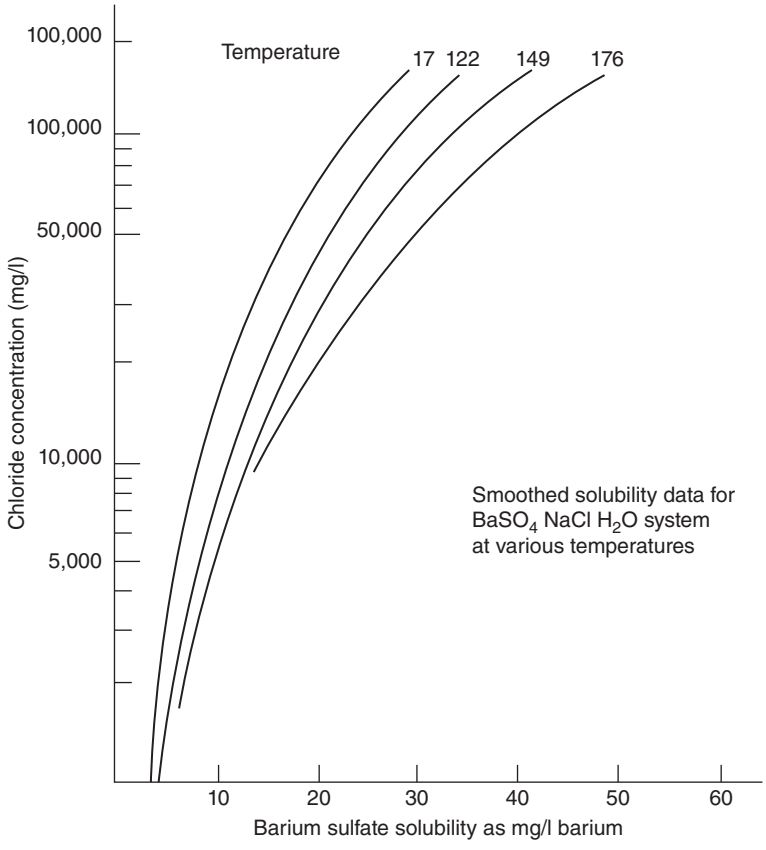


Figure 6.3 *Barium sulfate solubility as mg/L barium at various temperature (°C) and chloride concentrations (mg/L). (Reproduced with permission from Daubert Cromwell.)*

It can be used to determine the approximate conditions under which barium sulfate scale will form as shown in the following examples:

Examples

1. In a mixture of equal parts brine containing 40 mg/L of barium and 20.000 mg/L of chlorides with brine containing over 100 mg/L of sulfates and 1000 mg/L of chlorides, would barium sulfate scale form?

Answer:

Mixing the two brines would produce water that contained 20 mg/L of barium and 10.500 mg/L of chloride. The graph in Figure 6.3 shows that 20 mg/L of barium would be soluble only at the chloride concentrations and temperatures shown in Table 6.7.
Barium sulfate scale would form in an equal mixture of the two solutions described above.

Table 6.7 *Chloride concentrations and temperatures for given example*

Chlorides (mg/L)	Temperature (°C)
19000	80
25000	65
48000	50
60000	25

2. Would barium sulfate deposit from a mix containing 35 mg/L of barium and 100 000 mg/L of chlorides at 65 °C if it were allowed to cool to 25 °C?

Answer:

Yes, the solubility of barium is at its maximum at 65 °C. Any cooling of the water would lower the solubility and precipitate barium sulfate. ■

6.12.7.4 Testing

Table 6.8 offers a guide to the field identification of scales and probable causes. The use of this abbreviated chart is often complicated by appreciable amounts of oil and corrosion products being in the deposit. It is seldom possible to make a satisfactory examination of a scale which is oil soaked. After removal of most of the oil from compact scales, the criteria for tentative identification are usually made apparent by viewing with a hand lens and testing acid solubility.

The procedure to be followed in a complete laboratory analysis of the scale sample is given in Table 6.8. A Scale Analysis Report is shown in Table 6.9.

Weigh 2 g of scale sample into a 100 ml beaker. If the scale is white, you can proceed to test for $CaCO_3$ and then $CaSO_4$. If it neither dissolves in 1:1 HCl nor T-306, run a $NaCO_3$ fusion and test for Ba and Sr.

6.12.7.5 Paraffins

1. Boil the sample with benzene and decant.
2. Repeat step 1. until the benzene remains light in color.
3. Decant, dry and weigh.

Calculation:

$$\frac{100(\text{initial wt.} - \text{final wt.})}{\text{initial wt.}} = \%\text{wt.paraffin} \tag{6.31}$$

6.12.7.6 Acid Solubles

1. Total acid solubles: crush the dried residue and boil with 25 ml of 1:1 HCl. (At this point place a piece of moist lead acetate paper above the beaker. If it turns dark, FeS is present).
2. Allow the residue to settle and decant the acid into a graduated 250 ml beaker.
3. Repeat to ensure the $CaCO_3$, FeS or Fe_2O_3 has dissolved.
4. Wash with 25 ml. hot water and decant the water into the same 250 ml.
5. Dry and weigh.

Table 6.8 *Guide to identification of scales and probable causes*

Physical appearance	Acid solubility etc. (15% HCl)	Indicated composition and origin
1 White or light-colored:		
1.1 Hard, compact, fine granular	Insoluble	$BaSO_4$, $SrSO_4$, $CaSO_4$; incompatible waters
1.2 Compact, with long, pearly crystals	Powder dissolves slowly with no gas bubbles; solution gives SO_4^{2-} test with $BaCl_2$	Gypsum – $CaSO_4.2H_2O$. Incompatible waters or super saturation
1.3 Compact, fine grain or crystals which break into rhombohedra	Easily soluble in HCl with gas bubbles	$CaCO_3$ or mixture of $CaCO_3$ and $MgCO_3$ if more slowly dissolved; supersaturation, rarely incompatible waters
2 Dark-colored, brown to black:		
2.1 Compact, brown	Essentially insoluble; brown color dissolves on heating; acid turns yellow; white insoluble residue	See 1.1 and 1.2 above for white residue; brown, iron oxide is corrosion product or precipitate due to oxygen
2.2 Compact, black	Black mtl. dissolves slowly with evolution of H_2S, white insoluble residue	See 1.1 and 1.2 above for residue; black color is iron sulfide corrosion product, incompatible waters, or both.
2.3 Compact, brown or black	Easily soluble in 4% HCl (dilute 15% 1:4) with gas bubbles. Brown or black color remains	$CaCO_3$ with iron oxide or iron sulfide coloring matter
2.4 Soft muck, usually brown or black		
2.4.1	Insoluble	See 1.1 above
2.4.2	Dissolves, no bubbles	See 1.2 above
2.4.3	Dissolves, gas bubbles	See 1.3 above
2.4.4	Insoluble, except brown mtl., yellow solution	Iron oxide, see 2.1 above
2.4.5	Black material dissolves, evolution of H_2S	Iron sulfide, see 2.2 above

Discussion of inert residue and organic slime is omitted from the above outline. It should be emphasized that acid-insoluble residue occurs in all scale deposits, sometimes being the major ingredient. Also "soft muck" deposits may contain all the others, in a finely divided state, and their recognition may be difficult due to more or less organic slime.

Table 6.9 *Scale analysis, usual reaction of compounds, in solution in water, to form solid deposits*

$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$	Barium Sulfate, incompatible waters
$SrCl_2 + MgSO_4 \rightarrow SrSO_4 + MgCl_2$	Strontium sulfate, as above
$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 + 2NaCl$	Gypsum, carbonate, incompatible waters or supersaturation
$2NaHCO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl + CO_2 + H_2O$	Calcium carbonate, incompatible waters
$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$	Calcium carbonate, supersaturation due to pressure decrease, heat agitation.
$Fe + H_2S \rightarrow FeS + H_2$	Corrosion, iron sulfide may deposit or cause "black water"
$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O$	Inherent H_2S, or from corrosive bacteria, combines with iron oxide in solution or suspension

Calculation:

$$\frac{100(\text{wt.of benzene-insol.residue} - \text{wt.of acid-washed residue})}{\text{wt.of original sample}} \tag{6.32}$$

6.12.7.7 Iron Oxide and Calcium Acid Phosphate (Fe_2O_3 is usually brown, red, or black in color)

1. Dilute acid solution to 100 ml.
2. If a white precipitate flocculates when the acid solution is diluted, dissolve about 2 g of the original sample in 50 ml of conc. HCl and filter. Dilute the resultant filtrate to 100 ml, boil for 30 minutes, and add 5 ml of 5% sodium molybdate solution and 5 ml of amino solution while hot. Reheat to a boil and cool. A resultant blue color indicates the scale is calcium acid phosphate.
3. If the white precipitate does not appear, titrate this solution with 40% stannous chloride in hydrochloric acid, using a 2 ml pipette until the yellow color disappears. (If it changes after one or two drops, then it can be assumed there is no iron dioxide).

Calculation:

$$\frac{100(\text{ml } SnCl_2)(0.28)}{\text{wt.of original sample}} = \%\text{iron oxide} \tag{6.33}$$

6.12.7.8 Total Iron and Iron Sulfide (FeS is magnetic, black and sticky, and gives a positive test with lead acetate paper)

1. After adding the $SnCl_2$ solution to the end point in step 2, above, add one drop in excess.
2. Cool the solution and add 15 ml of saturated $HgCl_2$ solution.
3. Two minutes later add 50 ml of 50% phosphoric acid and six drops of diphenylamine sulfonic acid.
4. Titrate with standard $K_2Cr_2O_7$, 0.1913 M.

Calculation:

$$\frac{100(0.1)(\text{ml } K_2Cr_2O_7)(0.28)}{\text{total wt.of sample}} = \%\text{total iron as iron sulfide} \tag{6.35}$$

% Iron sulfide = Total Iron − % Iron Oxide (This can be done because the percentage of iron in iron oxide is nearly the same as it is in iron sulfide).

6.12.7.9 Asphaltenes or Sulfur

1. If the residue from the acid washing is black, ignite a portion of the original sample.
2. If SO_2 (from the acid odor) is formed, the residue is sulfur. Otherwise it is an asphaltene.
3. Estimate % by subtracting benzene and acid solubles and the weight of the residue after burning.

6.12.7.10 Calcium Sulfate

(If the scale consists of shiny white crystals, a qualitative test for $CaSO_4$ should probably be run first).

1. If asphaltenes or sulfur are present, burn the original sample and dissolve in hydrochloric acid to remove the acid solubles.
2. Place either this residue or the light residue from the acid treatment in boiling hydrogen peroxide. If the solid dissolves, $CaSO_4$ is present.
3. Also dissolves calcium sulphate, with the evaluation of gas.

Calculation:

$$\frac{100(\text{wt.of solid dissolved in } H_2O_2 \text{ or C-31})}{\text{wt.of total sample}} = CaSO_4 \tag{6.36}$$

6.12.7.11 Barium Sulfate and Strontium Sulfate

1. If the sample does not react in any of the above tests, then the scale is probably either barium sulfate or strontium sulfate, and a sodium carbonate fusion is necessary. Usually these samples are white.
2. Place the sample in a mortar with three times as much sodium carbonate by weight and 0.5 g KNO_3. Mix well with grinding, then transfer completely to a Coors crucible.
3. Place the crucible in a clay triangle and heat with a Meeker burner until the solids melt and the melt stops bubbling.
4. Cool the crucible and place in a beaker so that the crucible is immersed in a small amount of distilled water; boil until the sample becomes soft (tested by prodding with a glass rod).
5. Add four or five drops of HNO_3.
6. Place 6 ml portions of the liquid into two test tubes and acidify with a few drops of acetic acid.
7. To one test tube add five drops of potassium chromate solution. If a yellow precipitate forms, the scale is barium sulfate.
8. If a precipitate does not form, add five drops of dilute ammonium hydroxide, threedrops of potassium chromate, and heat it in a boiling water bath.
9. When hot, add dropwise with stirring, 40 drops of 95% ethyl alcohol.
10. Remove the tube, cool in a beaker of cold water and stir occasionally. A yellow precipitate means the scale is strontium sulfate. (The yellow precipitate can be tested by a flame test. A red flame is the check for strontium).
11. Theoretically the specific gravities of these substances are different but these determinations are unreliable because the densities are dependent on the way the scales are deposited.

7

Corrosion Inhibitors in Refineries and Petrochemical Plants

Corrosion in the hydrocarbon processing industries may be conveniently divided in to two parts: "wet" and "dry." Wet corrosion is that which occurs in the presence of liquid water. Corrosion in the absence of water is considered dry. Wet corrosion normally implies low temperatures, i.e. below the boiling point or dew point of water. This temperature will, of course, be a function of the system pressure, as well as its composition. In practice, wet corrosion is limited to about 232 °C (450 °F) as an upper temperature.

The lower temperature is set by fluid composition. For wet corrosion to occur at any temperature there must exist either a discrete aqueous phase or sufficient water dissolved in a liquid phase to impart electrical conducting or ionic properties to a liquid such as a hydrocarbon, which does not possess these properties in the absence of water. Wet corrosion is an electrochemical process. It may be controlled by the use of passivating, neutralizing, or adsorption-type inhibitors, the use of which will be summarized below.

Dry corrosion is of great importance in a number of refining processes. It includes the attack of hydrogen sulfide and other sulfur compounds on steel and various alloys at elevated temperatures (as distinguished from the attack of aqueous solutions of hydrogen sulfide and mercaptans). Solutions to this type of corrosion generally depend on metallurgical approaches, such as variations in composition and/or heat treatment of the selected metal or alloy.

7.1 Nature of Corrosive Fluids

Since the discussion of refinery and petrochemical plant corrosion inhibition will be restricted to attack taking place in the presence of aqueous fluids, the composition of these fluids is of interest insofar as it affects corrosion and its inhibition. Only fluids on the process side of equipment need to be considered.

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As an example, a heat exchanger in which naphtha vapors in the shell are being condensed by cooling water in the tubes may experience corrosion on both shell and tube side. Corrosion by cooling water and the attendant scaling and fouling problems are of great importance.

Restricting the discussion to process streams with an aqueous phase present, such streams may be considered as being composed of:

- an aqueous phase
- a hydrocarbon or non-aqueous liquid phase
- a gas phase.

The liquid and gas phases will be in dynamic equilibrium at all points in the system, the equilibria being determined by pressure, temperature, and composition. It will be useful to examine the general concepts of equilibria and composition.

7.1.1 Gas Phase

The gas phase consists of hydrocarbons vaporized by distillation processes and/or formed by cracking or other decomposition of fluids. Sulfur compounds, such as hydrogen sulfide and volatile mercaptans, often present in the gas phase, may be components of the original feed to the unit of interest, e.g. the crude still; they may be formed by thermal degradation of disulfides, thiophenes, etc., or they may be the result of various hydrogenation processes such as hydrodesulfurizing, hydrocracking, etc.

Prevention of air-leakage or other contamination is highly desirable and is effected by proper equipment maintenance, inert gas blanketing, etc. Prevention is rarely 100% effective in the practical sense.

7.1.2 Liquid Hydrocarbon Phase

This phase will be in dynamic equilibrium under the conditions of temperature, pressure, etc. with the vapor phase described above, as well as with the water phase contacting it. In this connection, it is of interest that the solubility of hydrogen sulfide and carbon dioxide in hydrocarbons is generally large compared to that of oxygen and nitrogen.

7.1.3 Liquid Aqueous Phase

Because electrochemical corrosion reactions proceed only in a liquid aqueous phase, the chemical composition and properties determined by chemical composition of this phase are most important to consider. This phase is largely water and will be called water in the subsequent discussion. Water enters the various refinery process units in a number of ways. Of prime importance is water that is entrained and/or emulsified in the crude oil charge to the refinery, i.e. the feed to the crude still. This water is produced with crude oil and remains with the crude, despite oil-field separators, liquid traps in pipelines, etc. Although the amount of water is usually small in total volume, its effect on corrosion may be large, since it usually contains a high proportion of corrosive dissolved salts, mainly chlorides of sodium, calcium, and magnesium.

7.2 Corrosion of Steel

Steel is very unstable in acids, as might be expected from the position of iron in the electromotive force series. In the absence of inhibitors, corrosion rates increase sharply as pH falls below neutrality.

At pH values above 7, steel is generally stable with increasing pH, up to values as high as 13 or greater. (At higher pH, particularly at elevated temperatures, attack results because of the weakly amphoteric properties of iron.) From a practical standpoint, neutralization of acid solutions to pH 6–8 normally is adequate to stifle direct attack on steel; however, when neutralization is augmented by inhibitors, adequate corrosion protection can be effected at pH values between 5 and 6 (The discussion above refers to reducing or oxygen-free systems, which refinery process streams usually are).

7.3 Corrosion of Copper Alloys

After steel, probably the most important metal in refinery use at low (i.e. less than furnace) temperature is copper, usually in the form of such alloys as Copper Development Association alloys No. 443-445 (Admiralty) or CDA 715 (Monel) etc. In addition to higher heat conductivity, copper and its alloys are considered to be superior in corrosion resistance to steel in media such as dilute acids, saline, and brackish waters, and in the presence of sulfur compounds. Because copper and its alloys have lower strength and versatility and cost more than low-carbon steels, substitution of steel by copper alloys must be justified in materials savings and/or process improvement.

Although copper is generally more resistant to acid refinery streams than steel, the effect of pH on corrosion of copper is more involved than on steel. Close pH control is necessary because of the dissolution of copper and its alloys at elevated pH under some conditions. At low pH, secondary factors such as presence of oxygen and fluid velocity are quite important in the corrosion of copper.

At high pH, in the presence of ammonia and some amines, soluble copper complexes form that effect copper dissolution.

7.4 Neutralizing Corrosion Inhibitors

Because corrosion is known to result from acid attack on metals, the removal or neutralization of acids is an obvious solution to the corrosion problem. In theory, any material sufficiently basic to neutralize the acid and raise the pH to the desired level should be satisfactory. In practice, the situation is complicated by other factors.

This is illustrated by operation of the desalter, which is usually the first processing unit in the refinery proper. Its function is to reduce the content of bottom sediment and water (BS&W) from the crude charge to the crude still. Water (generally brine) causes corrosion in units down-stream of the desalter as a result of decomposition of chlorides to hydrochloric acid at the elevated processing temperatures. Addition of alkali to the desalter reduces hydrolysis of calcium and magnesium chlorides and consequently results in less hydrochloric acid being formed in the crude still overheads, etc.

Inexpensive neutralizers such as lime, calcium carbonate, and soda ash often may cause scaling problems due to precipitation of insoluble hydroxides and/or carbonates of Mg and Ca by reaction with these ions in water entrained from the desalter. Sodium hydroxide can be used in desalting, for which it is added in amounts approximating the chloride content of the desalter water.

An attempt to establish alkalinity in the desalter by using high-pH boiler blowdown as desalter feed or high-pH effluents from sour water strippers is dangerous due to the problems of scale formation of Mg and Ca salts at high pH, and foaming at high alkalinity and/or in the presence of surfactants. This foaming causes poor water draw-off from the desalter, etc.

The first operating unit in a refinery after the desalter is the crude still, which effects a rough separation by boiling range of several refinery streams, such as naphtha, kerosene, diesel oil, etc. Distilled vapors are condensed at one or more points and products are taken off with the desired reflux

ratios, etc. The condensed liquids may contain dissolved acidic components such as hydrochloric acid and hydrogen sulfide, and will be corrosive to metals contacted by the liquids.

Corrosion may be expected as soon as the dew point of the water is reached, so treatment chemicals must be added at or upstream of the points of initial condensation. For treatment of overhead streams, ammonia and other low molecular weight amines such as morpholine or cyclohexylamine, which are added either as undiluted liquids or vapors, or as aqueous solutions, are recommended.

Ammonia is the most common material because of its high neutralizing power, low unit cost, easy availability, and convenience of handling. It may be injected as a liquid under cylinder pressure and flashed into the vapor phase of the crude still. Upon condensation of the vapors, ammonia will dissolve into the condensate water to effect an increase in its pH. As additional water condenses down-stream of the initial point, it will be in equilibrium with ammonia gas in the condensing hydrocarbon and water vapors.

Despite the advantages mentioned above, using ammonia has several drawbacks. Addition of ammonia beyond neutralization, i.e. pH to> 7, is a dangerous practice if copper alloys are present in the condensing system or down-stream of it in the water draw-off. At pH values in excess of 7 to 8.5 (depending on the source quoted), copper forms the soluble cuprammonium complex and deterioration of such materials as CDA 443-445 (Admiralty) can be expected.

Similarly, some of the low molecular weight amines also can form soluble copper complexes. Control of pH should be performed with automated measuring, recording, and feeding equipment, or by other means. The expense of such equipment can often be justified to plant management by savings in chemicals injected and in increased efficiency of corrosion control.

The use of higher molecular weight amines, which do not form chloride deposits from either the hydrocarbon or water phase, and which also have good buffering capacity compared to ammonia and morpholine is recommended. Such material permits easier pH control and largely eliminates the danger of copper corrosion at high pH (above 7.5 in the presence of ammonia or amines).

7.5 Filming Inhibitors

Refineries and petrochemical processes employ a variety of film-forming inhibitors under varying conditions. Due to the function of this type of inhibitor, they are generally more effective in the presence of an oil phase. In fact, it is often difficult to use filming inhibitors effectively and economically in the absence of an oil phase. Inhibitors are available with a wide range of solubilities and other physical properties. The concentrations at which they are used generally is about 10 ppm based on the hydrocarbon phase, so the economics are generally quite favorable.

The inhibitors most widely used in petroleum refining contain nitrogen bases such as amines, diamines, imadazolines, pyrimidines, and their salts, or complexes with fatty acids, naphthenic acids, and sulfonates. Inhibitors vary in solubility, etc., as mentioned above and also must be chosen in consonance with pH range and other fluid properties.

In general, it is more economical to reduce all or a portion of the acid content of treated stream with ammonia or another neutralizer, and augment this by use of a film-forming inhibitor.

Film-forming inhibitors, as distinguished from ammonia and other volatile amines, are considered to be non-volatile; accordingly, in any gas–liquid separation process, they remain with the liquid and so may be concentrated in the heavy fractions of a refinery process. The efficacy of an inhibitor treatment or other process changes in controlling corrosion should be followed in refinery work by use of corrosion test coupons or spools, corrosion rate meters, corrosion resistance probes and by analysis of process streams for dissolved metal.

7.6 Special Concepts in the Use of Corrosion Inhibitors in Refineries

Film-forming and/or neutralizing inhibitors in refineries offer no panaceas. Chemical treatment for prevention of corrosion is one of several tools used by competent engineering and management personnel as approaches to corrosion control alternative to other measures such as special resistant materials, protective coatings, design changes, and the like. Before discussing the relative advantages and disadvantages of the various protective and corrective measures, some limitations, as well as pitfalls to avoid, in using inhibitors will be mentioned.

7.6.1 Temperature Limitations

Film-forming inhibitors contain organic molecules with carbon–carbon, carbon–hydrogen, carbon–nitrogen bonds, and so on. In common with other organic molecules, they decompose at elevated temperatures. Inhibitors are recommended only for "low" temperatures, by which is meant corrosion in the presence of water. Furthermore, film-forming inhibitors act through an adsorption process, which generally becomes less effective at elevated temperatures, requiring larger treatment dosages to maintain effective films on metal surfaces. This increases expenditures for the treating chemicals. Above about 230 to 260 °C (450 to 500 °F) it may be said that film-forming inhibitors have limited application.

Fouling reactions occurring in the range of about 150 to 370 °C (300 to 700 °F) present problems, many of which are amenable to use of chemical anti-foulants. Above about 370 to 430 °C (700 to 800 °F), there is little experience to draw on in use of either film-forming or neutralizing corrosion inhibitors, or in the use of anti-foulants.

7.6.2 Insufficient Concentration

Many corrosion inhibitors of both the passivating and film-forming types (as explained in the chapter on inhibitor types) are classified as "dangerous," because they actually may produce increased localized corrosion and pitting compared to untreated systems if they are used in quantities insufficient to form an effective corrosion-resistant film. For this reason, it is not advisable to attempt reduction of inhibitor costs by reducing dosage below safe, effective levels.

If iron content is used to measure the results of inhibitor treatment, the initial rise when treatment is begun, usually attributable to cleaning of scaled surfaces, will soon fall to a rate less than that before treatment. If it does not, then either too little inhibitor is being used, or the inhibitor is not being added in such a way that it reaches the corroding equipment.

In actual plant practice, the inhibitor is normally added at concentrations of 5 to 10 times the final desired recommended value. The high concentration reduces the time needed for sloughing of old deposits and also accelerates the attainment of a good film on the cleaned metal. The concentration is gradually reduced after this, until the desired inhibition level (as shown by coupons, resistance probes, water analysis) is attained at an economical cost.

7.6.3 Surfactant Properties of Inhibitors

The effectiveness of film-forming inhibitors, as already stated, depends upon strong adsorption of inhibitor molecules at the interface between the process liquid(s) and the metal surface to be protected. It is not at all unusual for materials active at a solid–liquid interface also to be active at a liquid–liquid and/or a liquid–gas interface.

The former may cause emulsification problems, the latter may result in foaming. Emulsion problems are evidenced in water draw-offs in refinery equipment and in petrochemical plants, e.g. separation of oils and tars from ethylene quench water systems.

Of great importance when refining products such as jet fuels is emulsification of small quantities of water into the product. The water may enter the system because of storage tanks that "breathe" humid atmospheres or carry water bottoms, or by contamination or careless handling. Water that does get into the jet fuel storage system often is difficult to remove with settlers or coalescers when surfactants are present in the system.

Because of the deleterious action of emulsified water in promoting bacterial growth in storage, and in freezing and clogging of fuel injection nozzles during operation, jet fuel purchasers have strict requirements concerning such water, as well as the fuel response to it.

This is usually determined by the ASTM method D 2550-66T (Water Separometer Index, Modified or WSIM test). The WSIM test helps to find one inhibitor among the others that is effective as a corrosion inhibitor, but produces minimal emulsification or that can be modified by a demulsifying agent without losing its corrosion inhibitive properties.

7.7 Economic Aspects of Chemical Inhibition and Other Measures for Corrosion Prevention

In discussing various corrosion preventive measures, it is useful to consider that corrosion of the type described here, that is, attack by an aqueous liquid on a metal, has three prerequisites:

- an aggressive or corrosive liquid,
- an active or corrodible metal,
- intimate contact between the metal and the liquid.

The control measures available are to alter the metal or the environment, or to place a barrier between them to prevent their contact. Of course, combinations of two or more of these methods also may be applied for better results.

7.7.1 Altering the Metal

The activity of a metal may be changed somewhat by variations in its heat treatment or slight changes in composition; however, for marked differences in corrosion resistance, a completely different metal will generally be required. Thus, carbon steel may be replaced by copper or one of its brass or bronze alloys, or by one of several stainless steels or other alloys.

7.7.2 Corrosion Prevention Barriers

Various protective coatings, linings, claddings, and paints, are all examples of corrosion control by means of barriers separating the aggressive environment from the corrodible metal. While the cost of such systems is high (although rarely as high as resistant alloys) their life is limited.

Protective coatings and linings are usually applied over external surfaces and to internal surfaces of vessels of such size that the condition of the coating and lining can be observed visually at intervals, and defects patched or replaced. Accordingly, coating and lining breakdowns rarely result in catastrophic failure in refinery applications. Furthermore, coatings, particularly organic-based, should not be used under such extremes of temperature, pressure, and chemical environment as refinery alloys.

7.7.3 Altering the Corrosive Environment

The use of neutralizing amines for acid corrosion in refinery processing is an example of alteration of the environment. The use of filming amines may be thought of as a combination of environment alteration and a protective barrier, for example, the absorbed inhibitor film supplemented by the sorbed oil film. Chemical treatments employing neutralizers and/or filming inhibitors should be screened in the laboratory and tested in the plant to verify laboratory indications. Such tests are no more error-proof than those on metals or coatings.

In this respect, the advantage of chemical treatment is that the efficacy of treatment may be followed easily and cheaply in the plant and modifications quickly made if the original treatment is inadequate. Because of the sensitivity, rapidity, and ease of monitoring inhibitor treatments in the field, there is a small likelihood of substantial loss of equipment or performance, or of catastrophic failure. In general, all that is required is the use of a nominal volume of chemical, with appropriate feeding equipment and corrosion-measuring devices.

Probably one of the greatest economic advantages of chemical treatment over other methods is that the costs of chemicals that must be added continuously are treated for tax and accounting purposes as expensed items similar to maintenance and other operating costs. On the other hand, alloys, and coatings and linings systems usually call for capital outlays of considerable magnitude.

These expenses are not deducted directly from operating income and hence bear a less favourable tax position. Such generalizations, of course, may vary with individual companies and their accounting systems. Economic evaluation should be performed before selecting the type of corrosion preventive measure, because the success or failure of a corrosion prevention program depends on economic feasibility as well as on technical performance. A plant engineer who recommends a preventive treatment to his management should be conversant with economic evaluation and justification (see also Clause 13 Part 1 and NACE Standard RP-02-72, 1972).

In refineries and chemical plants with highly complex and inter-related processes and equipment, down time because of corrosion failure with concomitant loss in production, and product sales and profits, may be much more important than direct costs of equipment replacement or repair, and the labor to effect them. Such losses can easily exceed the cost of continuous treatment by corrosion inhibitors and anti-foulants.

7.8 Special Refinery Processes Amenable to Corrosion Inhibitors

The foregoing description has purposefully been kept as general as possible in order to illustrate the basic criteria for wet refinery corrosion and its solution by chemical treatment with neutralizers and film-forming inhibitors. Use of neutralizers and inhibitors has been described in the crude still and overheads. The same concepts can be applied in other systems where there is a hydrocarbon product in contact with liquid water containing corrosive constituents, usually hydrochloric acid and hydrogen sulfide.

Corrosion by naphthenic acids can be eliminated by them with neutralizing NaOH to form oil-soluble salts and the acid number of a crude containing naphthenic acids often gives an indication of its corrosivity during processing. This problem is not a major importance in refinery operations, where resistant alloys such as Type 316 stainless steel are used.

7.8.1 Hydrogen Blistering Problems

Hydrogen blistering problems are well known. The basic cause of hydrogen blistering is the trapping of atomic hydrogen in the interstices between grains of metal or at inclusions or laminations where

the atomic hydrogen combines to form molecular hydrogen. When the molecular hydrogen cannot escape through the metal surface, it causes blisters, cracking, and failure, etc., due to the increased pressure resulting from its formation.

Under most conditions of acid corrosion, the equilibrium between atomic and molecular hydrogen is displaced essentially completely in the direction of molecular hydrogen. However, in the presence of a number of catalytic agents, H atoms are kept from combining at the surface. Important catalysts are cyanides and sulfur compounds, including hydrogen sulfide. High nitrogen content in the feed stock appears to increase the probability of hydrogen attack in gas plants following catalytic cracking because of hydrogenation of nitrogen compounds.

In hydrocracking systems corrosion by aqueous effluents increases with the mathematical product of the nitrogen and sulfur contents of the water, which can be expressed as an equivalent content of ammonium sulfide. Total water volume, as well as fluid velocity, are also factors determining corrosion rates. Various parameters involved in corrosion in such systems and effect of pH, sulfide content, and cyanide content as competition between the formation of a protective iron sulfide film and its dissolution as soluble ferrocyanide.

This type of corrosion is becoming more common as hydrogen treatment processes proliferate. It is noteworthy that corrosion occurs at basic pH values, where it would be expected that iron and its alloys would be protected. A blue deposit of the ferro and ferrocyanides of iron in fouled or corroded equipment is often evidence of this sort of corrosion.

Both overall attack and hydrogen blistering may be effectively reduced by the use of "proper" film-forming amines. These amines are similar to be used for other refinery corrosion prevention services. It is very important that the "proper" inhibitor be used, as determined by preliminary laboratory and plant evaluation. This is because overall attack may be reduced, while blistering or hydrogen embrittlement may not if an "improper" inhibitor is used.

7.9 Corrosion in Gas Processing Units

Acid constituents such as carbon dioxide and hydrogen sulfide should be removed from natural gas in central field treating plants or in gas refiners before transmission of the gas for sale. Similarly, these constituents must be removed from plant gas streams, as in steam cracking of hydrocarbons for ethylene production, before the gases are subjected to low-temperature fractionation.

In the production of synthesis gas for subsequent conversion to ammonia or methanol, for example, it is usually necessary to remove carbon dioxide formed either by partial combustion of hydrocarbons or by the water gas shift reactions.

Gas treatment plants and gas refineries are bothered by corrosion problems. Much of these are caused by the breakdown of solvents, e.g. monoethanolamine, at the elevated temperatures of the reboiler regenerator. It is postulated that the breakdown products can chelate with iron and prevent the formation of an insoluble protective film at the high pH of operation, which should preclude corrosion of iron.

In this respect, there is a similarity between the corrosion of iron in amine solutions in gas regeneration, for example, and that in the effluents from hydrocracking plants described earlier.

Corrosion and other operational problems can be greatly reduced by proper plant operation. It is recommended that the gas loading (ratio of moles of acid gases to moles of MEA) be kept to 0.45 or less, monoethanolamine concentration be kept at 20%, and that degradation products be removed by use of a side-stream reclaimer.

Most of the authors quoted recommended maintaining reboiler temperatures at the lowest practical values in order to reduce solvent degradation and subsequent corrosion of equipment.

The use of sodium sulfite and hydrazine for removal of oxygen and reduction of the corrosion loading in the system is also recommended. Foaming, a common problem in many gas–liquid separation

or extraction processes, may be aggravated by surfactants, particularly in MEA systems and by fine particles, such as corrosion products, which act as foam nuclei or stabilizers. Use of a side-stream filter to remove these particles often is an effective supplement to the proper corrosion inhibition in solving such foaming problems.

The use of sodium metavanadate as a successful corrosion inhibitor in an MEA system removing carbon dioxide from hydrogen streams has been reported. Use of the inhibitor above 108 °C (225 °F) is believed to produce a highly protective film of Fe_3O_4.

Both potassium nitrate (0.5%) and potassium chromate (0.2%) are very effective in carbon dioxide systems, but not with hydrogen sulfide. Use of metavanadate in hot carbonate systems can passivate steel in a carbonate solution only when the bicarbonate content is low. The addition of oxygen to the system increases passivation of mild steel, but increases corrosion of copper–nickel alloys.

7.10 Miscellaneous Refinery Corrosion Problems

Many miscellaneous corrosion problems in refinery and petrochemical plants involve metal contact with strong acids, such as sulfuric used in alkylation and acid washing, hydrofluoric in alkylation, nitric from ammonia oxidation, and so on.

Generally these corrosion problems are solved by means other than the use of corrosion inhibitors, e.g. by changes in process design (such as assuring water-free systems, or by maintaining sulfuric acid at sufficiently high concentrations to be non-corrosive to steel); by metallurgical approaches and selection of resistant alloys; by use of protective coatings and linings; or by anodic protection.

Corrosion prevention by chemicals is not ordinarily practical in refinery work for acids that are either concentrated or strong. However, dilute acid streams often may be rendered non-corrosive by use of inexpensive neutralizers and/or filming inhibitors. Examples include the mixed condensate composed of water and hydrocarbon liquids from dehydrogenation of ethyl benzene to styrene in the presence of steam, various acidic wash streams, etc.

In using inexpensive and easily available alkalis for neutralizing acidic streams, washing out vessels, etc., the chloride content of the commercially available soda ash or caustic must be carefully controlled, as must the chloride content of the plant or source water used to make up the neutralizing and wash solutions. This is because of the deleterious effect of chloride ions in destroying passive films on normally corrosion-resistant alloys, such as the various types of stainless steels, resulting in stress corrosion cracking (SCC) of these materials. A NACE publication by L.T. Overstreet, "Recommendations for the Use of Neutralizing Solutions to Protect Against Stress Corrosion Cracking of Austenitic Stainless Steels in Refineries, Report of NACE Committee T-8-6, Proceedings of the 25th NACE Conference, NACE, Houston, Texas, 578–582 (1969),"which discusses this problem and gives detailed recommendations should be followed.

With increasing use of stainless steels in a wide variety of services, the problem of stress cracking has deservedly received a great amount of attention. Various parameters influencing SCC have been found in systems where hydrogen sulfide is a principal causative factor. Among them are strength of steel, stress level, and acidity or alkalinity of the environment. Low pH is very detrimental regarding the stress corrosion cracking of high strength steel, with a considerable increase in resistance to SCC as the pH is raised from 2 to 5.

Hydrodesulfurizer units, etc., in refineries face the presence of hydrogen sulfide and polythionic acids formed by reactions between hydrogen sulfide and sulfur dioxide. Air increases susceptibility to SCC in these systems, as it is also known to do in systems where chloride is the principal causative factor. Chemical agents can be used for prevention of stress cracking by alteration of the environment, e.g. by changing the pH or by use of anti-oxidants for removal of oxygen. Although the principal means of preventing SCC is by controlling the environment as described above or by alteration of the metal, protection by barriers can be used, provided they can be kept intact.

This is usually difficult with protective coatings; however, it may be effected by use of films formed by inhibitors, which are in dynamic equilibrium with liquids containing inhibitor and in contact with the metal to be protected. Hence, the film can be repaired continuously. Use of film-forming inhibitors also reduces failure by corrosion fatigue, a phenomenon similar to stress corrosion cracking. Fatigue can increase by a factor of as much as 10, depending upon the inhibitor used and the conditions of filming. The efficacy of the various treatments described is attributed to the strength of the film and its insolubility in the filming and contacting fluids. This would appear to indicate the potential of applying film-forming inhibitors for prevention of stress cracking and corrosion fatigue in refinery as well as down-hole applications.

7.11 Selection of Inhibitor

7.11.1 Test Methods

Irrespective of the method, it should be remembered that the relative corrosion rate before and after treatment is used as a basis of comparison. This is generally easier to determine and of more use than the absolute rate. It is also important to consider that the build-up, breakdown, and repair of films formed by adsorption-type inhibitors are not instantaneous processes, but may require times of the order of several days.

Accordingly, the limitations of spot readings, as determined by electrical corrosion rate meters and "grab" samples of fluids for metal ion analysis must be considered. In addition, because a corrosion rate meter gives readings only in electrically conducting media, readings are dependent on the conductivity of the medium and suitable corrections must be made for stream composition and/or conductivity.

Process stream analyses for dissolved metals such as Fe^{2+}, Cu^{2+} among others, can be carried out quickly and cheaply, but are of questionable value in streams containing hydrogen sulfide, because its corrosion products usually will be insoluble sulfides.

Obtaining a representative and reliable sample of the stream is difficult under such conditions. In addition, because of their detergent action, many inhibitors often cause an initial increase in the amount of sludge and scale going into the process stream, as old deposits are loosened by the detergent-inhibitor and slough off equipment. This increase must be recognized for what it is and not be assumed to signify an increased corrosion rate.

Test coupons are the most widely used tool in monitoring refinery corrosion and its treatment because they may be easily prepared, inserted, removed, and evaluated. Coupons are composed of metals similar to those of interest and exposed to similar conditions.

Accordingly, coupon exposure times are generally 2 to 4 weeks for determination of "before" and "after" conditions. Exposure time will be limited and data questionable if process changes are made during the exposure period. Such variations as changes in feed stocks, processing charge rates, temperatures, and the like may affect corrosion rates sufficiently to negate the effects caused by changes in the inhibitor program under investigation.

7.12 Control of Fouling

Despite long use, the meaning of the word "fouling" remains nebulous. In this book, fouling is considered to relate to the presence of solid materials, without respect to origin and nature, that are insoluble in the process streams of interest. These materials cause operating difficulties by deposition onto surfaces of equipment contacted by the process streams, either in zones where the insolubles are formed

and/or in down-stream units. Such deposits interfere with mass and heat transfer, as evidenced by reduced heat transfer coefficients and flow rates and by increased pressure drops.

Accordingly, throughputs are reduced, while pumping costs and heating or cooling requirements are increased. In extreme cases, fouling may result in complete plugging, or burning out or rupturing of critical process units. Thus, the scope of fouling problems is seen to be quite broad.

7.12.1 Inorganic Fouling Deposits

It is sometimes useful to classify fouling deposits by their inorganic or organic nature, because such a classification may point to the cause of the fouling and indicate possible methods of prevention or alleviation. Corrosion products such as metallic oxides and sulfides may deposit on equipment down-stream of the area of corrosive attack, causing fouling problems. Use of corrosion inhibitors to solve the corrosion problem is a possible solution to the fouling problem, due to the existence of an interdependence between fouling and corrosion in process equipment.

Another common fouling problem due to inorganic deposits may occur when ammonia is used to neutralize HCl formed by hydrolysis of chlorides after crude desalting. Increasing the pH, in order to reduce corrosive potential, results in formation of the oil-insoluble salt, NH_4Cl. This may result in a fouling problem that can be alleviated by adding water to the affected unit, either continuously or intermittently.

Another approach is to reduce the amount of ammonia added for neutralization and operate at a lower pH, and instead use organic film-forming inhibitors to control corrosion. The frequency of this approach has increased because of the development of inhibitors active over a wider pH range than those originally used in refinery work.

A third solution to the problem employs neutralizers other than ammonia, e.g. morpholine, cyclohexylamine, or other high molecular weight amines, which combine with mineral acids to give salts having higher oil solubility and/or dispersibility thanNH_4Cl.

7.12.2 Organic Fouling Deposits

Organic fouling is much more prevalent, but less well understood than inorganic fouling. Usually, organic foulants are high molecular weight materials formed by oxidation, polymerization, or other reactions of constituents in the process streams. These constituents may be the principal components of the streams or impurities within them. Deposits range in consistency from rubbery-like solids to “pop corn” and coke. Deposit, as well as stream, analyses may be of value in determining the composition of the deposit to indicate its origin and remedy. However, such analyses are often time-consuming, expensive, and do not yield a great deal of useful information. Nevertheless, some useful generalizations can be made on factors influencing fouling and possible methods of prevention. Several examples will be discussed below.

It should be emphasized that although the term paraffin (low affinity) implies that such materials are non-reactive, this is not necessarily the case at the elevated temperatures and pressures involved in petroleum processing, and in the presence of certain contaminants. Paraffins are relatively non-creative, compared to other more active components such as olefins, aromatics, and heterocyclic hydrocarbons encountered in petroleum refineries and particularly in petrochemical operations. The presence of such reactive materials, even in the range of parts per million (often beyond the scope of conventional stream analyses) can lead to severe fouling. Consideration must be given to the effect of ppm concentrations multiplied by stream volumes of thousands of barrels per day, and continuous operation for months to give large quantities of deposits from streams containing only minute concentrations of foulants.

Operating parameters such as temperature, pressure, and contact time, all of which increase fouling reaction rates, ordinarily are set by processing conditions. Additional factors are stream

contamination effects, which may or may not be amenable to process changes. Many fouling reactions proceed through free-radical oxidation and polymerization routes, so that the elimination of free radicals or their precursors is desirable.

Because oxygen is effective in many free-radical reactions, prevention of air contamination in a system is desirable. This is accomplished by "tightening up" the system, minimizing transfer and storage times, and/or by such procedures as inert gas blanketing of storage vessels. Many materials are so sensitive to traces of oxygen, however, that even these measures allow some fouling to occur. Consequently, antioxidants may be used to negate the effect of air.

Another factor that increases fouling is the presence in the process streams of trace quantities of certain active metals such as iron, nickel, vanadium, and particularly copper. These metals are present because of their original occurrence in the crude streams, or from corrosion of process equipment constructed from the metals or their alloys. Surfaces of these metals are also active catalysts for fouling reactions. Here again, the interdependence of corrosion and fouling is illustrated, since metal contaminants resulting from corrosion in up-stream units may be reduced by the use of corrosion inhibitors.

Oil-soluble dispersants are widely used to alleviate both organic and inorganic fouling problems. The object is not to prevent the initial formation of coke nuclei and other insoluble particles in the stream, but to reduce their tendencies to agglomerate into larger precipitates that can settle out of the process stream and deposit on and in various places in the equipment. A test for effectiveness of materials as anti-foulants, based on their ability to disperse carbon black in hydrocarbons can be established.

Commercial materials recommended for use as anti-foulants in processing industries contain combinations of dispersants, anti-oxidants, metal deactivators, and/or corrosion inhibitors. The choice of the best material for a given application should be determined by effectiveness and cost. Screening tests to differentiate between alternative materials will be described below. Because of the wide variety of streams requiring treatment, many commercial anti-foulants have been developed for different applications. The situation is similar to that of corrosion inhibition and no universal remedy is available.

An additional important property of anti-foulants is high-temperature stability. Temperatures above 200 °C (400 °F) are common and applications in the range of 315 to 345 °C (600 to 650 °F) are not unusual.

Higher temperatures also may be possible for very short contact times. Applications of anti-foulants are being attempted under extreme conditions such as in ethylene steam-cracking pyrolysis units. The surface of the pyrolysis furnace tubes may be altered by the anti-foulant so as to reduce the catalytic effect of the surface in promoting coke formation.

7.12.3 Use of Anti-Foulants

Principal uses of anti-foulants are in hydrodesulfurizers (for naphtha, gas, and lubricating oils), in naphtha reformers, in crude and catalytic cracking units. Other units include cokers, visbreakers, alkylation units, ethylene units, deethanizers, solvent recovery units, etc. While fouled equipment consists primarily of heat exchangers, furnace tubes, piping, and distillation towers can also be affected.

The economic justification for using an anti-foulant is usually based on how it increases on-stream time, improves heat transfer efficiency, reduces fuel costs, improves fluid throughput, and the like.

Costs of cleaning, repairing, and replacing fouled equipment are generally of secondary importance. All direct and indirect costs must be balanced against the cost of the treatment program used for fouling prevention or alleviation.

7.12.4 Evaluation of Anti-Foulants

Despite the effectiveness of anti-foulants used in relatively small concentrations (5 to 20 ppm) and the modest unit cost of the chemicals, total costs can be appreciable because of the large volume of

streams treated. It is desirable to optimize the cost versus effectiveness of the treatment by selecting the best additive(s) for the specific application under consideration. Because of the wide diversity of refinery and various petrochemical streams, no single approach or chemical may be expected to be a universal solution to all fouling problems.

Due to the cost, as well as time, in testing anti-foulants in plant applications, some laboratory test methods have evolved to determine the fouling potential of process streams and to evaluate the effects of alternative additives and treatment levels. These laboratory tests are always of relatively short duration – from several minutes to several days – and require intensification of the causative factors to increase fouling rates, and thus provide measurable changes in the system parameters during the test times, which are short relative to the weeks or months of actual field fouling problems.

Temperatures may be higher, contact times longer, or contaminant levels greater (e.g. by blowing air into the test fluids). Because of the more severe conditions of the tests, additive levels are usually higher than under plant conditions. Several screening tests described below illustrate these concepts. It is important to remember that these tests are for screening rather than for prediction of additive performance under actual field conditions, which may be very much different from the test conditions.

Accordingly, the screening test should be used only to obtain preliminary information on materials that appear promising on a cost–performance basis. Promising materials should then be evaluated in the field for optimization of the anti-foulant treatment.

7.12.4.1 Erdco CFR Coker Test Method

This method is a modification of the Erdco jet-fuel testing procedure (ASTM D-1660). In this unit, the test fuel is pumped at a controlled rate over a heated surface 204 °C (400 °F), which is designed to simulate feed preheat exchanger conditions. Decomposition of materials in the process stream on the hot surface causes deposition of polymers and coke, some of which adhere to the surface.

However, some decomposition products also are carried in suspension by the fluid stream, which is then pumped through a metal filter having 20 μm pores. These capture much of the suspended matter from the stream. Because suspended matter plugs the filter, the pressure across it rises exponentially with time. The slope of log pressure drop versus time is used as a measure of the fouling index, which has been correlated with plant fouling conditions for both treated and untreated conditions.

In ASTM D-1660, the physical appearance of the heat transfer surface, i.e. blackening and coking, is expressed in a quantitative manner to correlate with fouling tendencies of heated jet fuels, etc.

7.12.4.2 Jet-Fuel Thermal Oxidation Tester

Better correlation between test results and refinery experience with anti-foulants is claimed with data from the Jet-Fuel Thermal Oxidation Tester (JFTOT) developed by a San Antonio, Texas firm. The device operates on the same principles as the Erdco coker developed in 1965 by Amoco, and according to ASTM D-1660. One of the main advantages of the JFTOT tester is that it uses only one quart of fuel.

Because JFTOT and Erdco produce much the same sort of data, data from JETOT can be posted on Erdco data sheets.

7.12.4.3 Other Methods

There are numerous variations on the above methods. The “hot wire” is a fairly simple and inexpensive test that employs heating of the test fluid by contact with a hot nichrome wire. The wire is heated by a current (about 5 to 10 amperes) sufficient to elevate the temperature to incipient redness. As the fluid decomposes on the hot metal surface, fouling may be observed by:

- An increase in the apparent diameter of the wire as coke covers the wire.
- Discoloration of the liquid.

- Changes in the current through the wire brought about by reductions in thermal and electrical conductivities. Normally, several determinations are carried out simultaneously with the test wires in series electrical connection. Thus, the treated and untreated systems can be compared visually and followed with time.

Field methods used to follow the course of fouling and its reduction by various treatments are based on changes in operating parameters. Because fouling usually reduces fluid flows and decreases heat transfer rates, but increases pressure drops and heating (or cooling) demands, all of these or the rates of their changes in the treated and untreated systems may be used as indications of the effectiveness of the treatment. However, it should be noted that many of these parameters can also be changed by process variations independent of fouling, e.g. changes in charge rates, cracking severities, feed stocks, etc. Accordingly, tests that are carried out for extended times require careful control and data interpretation.

Other methods of rapid evaluation in laboratory and/or field are proposed from time to time because of the need for a guide and an accurate screening method for anti-foulants. These methods should be considered as to their ability to measure true fouling rates or fouling potentials, or some other physical or chemical property purported to be related to the desired property. When extrapolating the test conditions to the field conditions, it should be remembered that the dangers in such extrapolations increase as the conditions between actual and test conditions diverge.

A summary of present day laboratory and field methods of evaluating anti-foulants was presented during a round table discussion in a September, 1971 meeting of the NACE T-8 (Refinery Corrosion) Committee in Chicago.

An additional concept in the evaluation of anti-foulants by laboratory screening devices has been pointed out by Nathan and Dulaney. This concept considers the wide fluctuation in reproducibility of test data obtained at intermediate efficiency values of additive applications. At low efficiencies, such as those obtained at low treatment levels, or at high efficiencies, such as those obtained at high treatment levels, replicate tests have good reproducibility.

However, poor reproducibility at intermediate concentrations and efficiencies limits the ability to differentiate between the cost-effectiveness of alternative additives. Similar difficulties have been reported with respect to the evaluation of corrosion inhibitors in refinery processes and other applications and in testing the effect of surfactants employed as corrosion inhibitors and/or anti-foulants on the water tolerance of jet fuels (WSIM test). The limitations of screening tests emphasize the inadvisability of undue reliance on them and the need for following such tests with careful plant studies to obtain reliable technical and economic data on anti-foulant applications.

7.13 Utility (Cooling Water and Boiler Systems)

7.13.1 Corrosion Control in Cooling Water Systems

Evaporation is the chief source of cooling in a recirculating cooling water system. As it proceeds, the dissolved solids (e.g. the mineral salts) content of the water increases until solubility considerations necessitate its limitation (i.e. by blowdown). Intimate contact of the circulating water with the atmosphere is provided by the cooling tower or spray pond in order to facilitate the evaporation. This keeps the dissolved oxygen content of the circulating water near saturation. Both of these factors, high content of salts and high dissolved oxygen level increase the corrosivity of the cooling water. Cooling water systems usually consist of a number of dissimilar metals and non-metals. Metals picked up from one part of the system by the water tends to deposit elsewhere in the system on contact with more anodic components. This produces galvanic couples that further aggravate the attack.

Corrosion control in cooling water systems involves good design and materials selection, as well as good fabrication, installation and operation. Complete corrosion prevention by materials selection

requires expensive materials such as stainless steels. Materials commonly used in a cooling water system are carbon or low-alloy steel, copper alloys, stainless steels, aluminum and wood.

Substitution of carbon or low-alloy steels in cooling water systems for those of more expensive materials results in marked savings in initial costs. Use of cheap materials can increase the costs of operation, including water treatment and inhibitor application. A compromise between the cost of construction, materials, and operation should be performed at the design stage.

7.13.1.1 Economics of Cooling Water Corrosion Control

The principal economic advantages for the treatment of cooling water system come from two sources:

1. It reduces frequency of maintenance and inspection shut-downs.
2. It permits more extensive use of iron and carbon or low-alloy steel instead of high-alloy steel and copper alloys.

Production losses during shut-downs are the major economic concern. The frequency of periodic shut-downs for maintenance and inspection depends on the reliability of the corrosion control program. The more corrosion control applied, the fewer shut-downs will occur in the system. Thus, less time is lost from scheduled shut-downs. The frequency of costly, unscheduled outages can reduce even more drastically.

7.13.1.2 Justification for the Use of Inhibitors

Substitution of carbon or low-alloy steel tubes for those of more expensive copper alloys in heat exchanger service results in marked savings in the initial costs. Because Admiralty tubes are roughly 60% more expensive than carbon steel, the designer must be assured of reasonably long and trouble-free service if the additional cost of the copper alloy tubing is to be justified. The tubes must resist the build-up of corrosion products that will interfere with heat transfer and flow, as well as accelerate the development of leaks.

Treatment of once-through cooling water with inhibitors is too costly for frequent use. Replacement of steel tubes because of their limited useful life in once-through systems is accepted as a necessary addition to the cost of the cooling operation. One alternative is use of more expensive alloy tubes. However, it is important to recognize the importance of growing concern regarding thermal contamination of the environment, which indicates that once-through systems for other than, perhaps, seawater cooling will not be acceptable for much longer.

7.13.1.3 Problems with Blowdown Disposal

The disposal of blowdown from recirculating cooling systems also poses environmental contamination problems. Inhibitors and process contamination are the major concerns, although excessive dissolved solids may prove objectionable in some cases. A number of the major components now used in cooling water inhibitors must be removed before blowdown is acceptable for disposal in surface supplies (i.e. lakes and streams). Cost of this removal must be included in economic evaluation of inhibitor treatment. Alternative, environmentally innocuous inhibitors, may be used for satisfactory corrosion control. Corrosion inhibitors alone probably account for 60 to 70% of the total.

In addition to NACE Standard RP-62-72, for more details of the economics of corrosion control in recirculating cooling systems see Economic Data on Chemical Treatment of Gulf Coast Cooling Waters, Corrosion, 11, 61–62 (1965) Nov., reported by the NACE Recirculating Cooling Water Sub-Committee.

7.13.1.4 Selection of Inhibitor

For treatment of cooling water systems and selection of inhibitor(s), in addition to this book reference is made to the NACE publication “Corrosion Inhibitors” edited by C.C. Nathan.

7.13.2 Corrosion Control in Boiler Systems

Corrosion in boiler systems cannot be isolated entirely from a number of other concomitant problems that have a direct effect on the type, amount, and location of corrosion, and the functioning of the boiler. These problems, which are considered along with corrosion, can be identified as scale, sludge and carryover.

There are a number of locations in a boiler system where various types and amounts of corrosion can occur. These locations can be grouped in three generalized locations: preboiler, boiler, and postboiler.

7.13.2.1 Preboiler Corrosion Problems

The preboiler system is defined here to include feed water pumps and lines, and auxiliary equipment through which the feed water is pumped prior to actually reaching the boiler. If not restricted, one could include a vast variety of units in which the makeup water is conditioned, but which in themselves are not essentially a part of the boiler system. This definition then includes such equipment as stage heaters and economizers.

Using this definition, one finds both corrosion and deposit problems in the preboiler system that can manifest themselves as general corrosion, pitting, or erosion-corrosion. The deposit problem can result from either deposition of suspended solids that should have been removed earlier in the clarifier unit, or else it may be caused by formation of adherent calcium, magnesium, or iron scales.

7.13.2.2 Corrosion Effects

Corrosion can attack iron, copper, or nickel. General corrosion or pitting may occur for conventional reasons, e.g. dissolved oxygen, low pH, presence of deposits, stagnant areas, stress in the metals, defects in metal composition, or surface conditions. Dissolved oxygen often will cause pitting attack when coupled with certain other conditions, such as deposits on the metal surfaces or metal defects.

Acidic pH values will lead to general corrosion; the other factors will generally favor localized attack. Cavitation-corrosion can be encountered in the pumps or at other locations where turbulent or high-velocity flow may occur. Stage heaters and economizers are designed to increase the feed-water temperature, which will increase the operating efficiency of the entire system, and, as the temperature is increased, susceptibility to corrosion is also greatly increased.

7.13.2.3 Sources of Deposits

There are two major sources of deposits in the preboiler system. These are identified as: (a) suspended or (b) dissolved. Suspended solids are the mud or silt commonly found in surface water such as that from lakes or streams. These suspended solids should be removed from the water by the clarification equipment before it enters the preboiler system. However, improper operation of such equipment may result in suspended solids entering the system. The standard coagulation process may employ lime, which removes some of the hardness and changes the alkalinity balance of the water. Additionally, suspended turbidity, such as clay particles, is removed from the system.

Additional coagulants, such as high molecular weight polymeric materials can be used, as can aluminum salts or sodium aluminate.

The residence time in the clarifiers should be sufficient and the filters should function properly, so that no fine floc particles are carried through to the preboiler system where they can settle out and cover the lines with deposits. The particles that do not settle out in the lines go to the boiler system and cause trouble there.

The other major source – dissolved solids – is common to practically all aqueous systems and will result in the formation of calcium, magnesium, or iron scales. Tightly adherent calcium carbonate or phosphate, magnesium hydroxide or silicate, or deposits of iron compounds are laid down on the

metal surface, interfere with heat transfer and set the stage for localized pitting. Deposit composition varies widely and is a function of the water constituents and temperature.

Phosphate deposits present a real anomaly. On one hand, polyphosphates are deliberately added (as will be shown later) to prevent adherent deposits and on the other hand, their reversion product, orthophosphate, can cause undesirable deposits. For this reason, temperature and pH conditions that accelerate reversion of polyphosphates must be considered carefully.

Economizers can present additional deposit problems. These units are designed to take boiler stack gases at about 480 °C (900 °F) and reduce them to temperatures approaching the dew point. In most cases, temperatures are in the range 138 to 204 °C (280 to 400 °F). Since relatively low-temperature gases are involved, it is necessary to design the economizer with a comparatively large heating surface and this usually results in low feed-water flow rates in the units. The low rate of flow combined with the increase in feed-water temperature – sometimes approaching boiler water temperature – can lead to severe deposition problems.

7.14 Boiler Corrosion Problems

General problems in boilers are deposits, carryover, and corrosion, which are common to most systems.

7.14.1 Deposits in Boilers

Deposits in boilers can be considered in two major categories: sludge and scale. The usual way to tell the difference between them is by the nature of their adherence. Scale is commonly thought of as being tightly adherent to the metal, while sludge may be dispersed in the boiler water, can be spread on the metal surface, from which it is easily removable, or else it can possibly serve as a binding agent for scale.

Sludge is often created deliberately. For example, orthophosphate is added to boilers as an "internal treatment" with the objective of precipitating all the calcium and magnesium in the form of easily removable sludge. An example of sludges that are not desirable, on the other hand, are organic compounds, which may result from contamination of feed water during passage through planted areas.

Oil contamination of feed water causes a sludge that adheres to the boiler walls and is difficult to remove. The formation of sludge balls can be encountered when the binder is a corrosion inhibitor, a paint residue, a fuel oil, or a lubricant. These sludge balls can become very large under some turbulent conditions. Severe attack by sludges may result on carbon steel and even on Monel.

A chemical analysis of the scales will only identify the chemical composition, so, for positive identification of the crystalline nature of consituents, X-ray diffraction must be employed. Table 7.1 shows scale constituents of deposits from high operating-pressure boilers that have been identified by X-ray diffraction.

7.14.2 Problems from Carryover

Carryover from boilers can be defined as the presence of water in the steam leaving the boiler. This water contains solids that cause deposit and corrosion problems in the postboiler system, one of the more serious of which is the rapid build-up of silica deposits on turbine blades. The silica concentrations are so critical that saturated steam is not safe for turbine vanes unless it contains less than 10 to 15 ppb SiO_3^{2-}. The problem of silica deposits on turbine blades is primarily present under high-pressure conditions, whereas at lower pressures a considerable amount of SiO_2can be tolerated in the boiler water. At pressures over about 27 to 41 bars (400 to 600 psig), silica in the boiler water

Table 7.1 *Crystalline scale constituents identified by X-ray diffraction*

Name	Formula
Acmite	$Na_2O.Fe_2O_3.4SiO_2$
Analcite	$Na_2O.Al_2O_3.4SiO_2.2H_2O$
Anhydrite	$CaSO_4$
Aragonite	$CaCO_3$
Brucite	$Mg(OH)_2$
Calcite	$CaCO_3$
Cancrinite	$4Na_2O.CaO.4Al_2O_3.2CO_2.9SiO_2.3H_2O$
Hematite	Fe_2O_3
Hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$
Magnetite	Fe_3O_4
Noselite	$4Na_2O.3Al_2O_3.6SiO_2.SO_4$
Pectolite	$Na_2O.4CaO.6SiO_2.H_2O$
Quartz	SiO_2
Serpentine	$3MgO.2SiO_2.2H_2O$
Thenardite	Na_2SO_4
Wallastonite	$CaSiO_3$
Xonotlite	$5CaO.5SiO_2.H_2O$

Table 7.2 *Steam purity*

Operating boiler pressure, bar (psi)	Total, ppm		Suspended solids
	Solids	Alkalinity	
0–20 (0–300)	3500	700	300
20–30(301–450)	3000	600	250
30–40(451–600)	2500	500	150
40–50(601–750)	2000	400	100
50–60(751–900)	1500	300	60
60–70(901–1000)	1250	250	40
700–100(1001–1500)	1000	200	20
100–136 (1501–2000)	750	150	10
136 and higher (2001 and higher)	500	100	5

will vaporize and contaminate the steam. As pressure is reduced as steam passes through the turbine, the silica begins to deposit, causing reduced turbine efficiency.

If salt mixtures such as sodium chloride, sodium sulfate, or sodium hydroxide are carried out and form deposits, then corrosion occurs, especially if the melting point of the mixture is lower than the steam temperature. Deposits of copper and its oxides can also cause corrosion.

The American Boiler Manufacturers Association has established standards for boiler water balances in its standard steam purity guarantees. These are identified as "ABMA Limits" and are listed in Table 7.2.

The carryover can occur as a result of mechanical or chemical causes. Carryover is generally classified as foaming, priming, or general entrainment in the steam. Some of the mechanical factors that influence boiler water carryover are:

1. Boiler design
2. Severe steam load swings
3. High water level.

The foaming problem is the most difficult to control and can be caused by a number of factors. Some of the major ones follow:

- Oil contamination
- Other organic or collodial contamination
- High total dissolved solids content
- High alkalinities
- Suspended solids.

Maximum limits for oil in boilers shall be of 7 ppm or less than 1% of suspended solids. At constant loading of a boiler the height of the foam rises with the salt content of the boiler water. The nature of the salt is important: Na_2CO_3has a greater effect than NaCl orNa_2SO_4. Foam can be caused by solid carbonates that are present due to evaporation of feed water or dislodged incrustants.

7.14.3 Corrosion Problems

The corrosive factors in a boiler vary, but in a broad sense they can include dissolved oxygen, high temperatures and pressures, high salt concentrations, high heat transfer conditions, stresses, localized concentrations of caustic (boilers are purposely operated at high pH values), erosion, peculiar localized flow conditions, deposits of salts, metals, and metallic oxides, and scales and sludges with localized overheating. The materials of construction are invariably carbon steel or low-alloy iron and steel, except in nuclear boilers, where alloys may be used. Various types of corrosion that can be encountered include pitting, concentration corrosion, caustic embrittlement, stress corrosion, erosion-corrosion, and, in nuclear installations, mass transfer.

7.14.3.1 Stress Corrosion

Caustic embrittlement is actually only one type of stress corrosion cracking. It is the one most frequently found in boilers and for that reason merits special consideration.

The most likely place for cracking to occur is in a stainless steel tubed steam generator, where high chloride concentrations and steam-blanketed areas develop. In addition, considerable free oxygen is likely to be present. Oxygen has an adverse effect on chloride stress corrosion, and both oxygen and chloride must be present for stress corrosion to occur.

The problem of stress corrosion cracking becomes especially severe for those stainless steel parts that are intermittently exposed to boiler water. This exposure represents a much more severe condition for inhibition than in the case of parts that are submerged in water continually. Cracking in the parts that are in the vapor phase does not occur if water containing chloride does not come into contact with them by splashing or by some other mechanism.

7.14.3.2 Erosion-Corrosion

On occasion, failures that occur in boiler tubes can be attributed to an erosion mechanism. They generally occur at areas in the tubes where the normal direction of flow has been altered abruptly, a condition of turbulence created and a new flow path followed. The resultant corrosion is similar to that found in some feed-line systems. Here again a situation exists where the primary cause of the failure is a physical one, i.e. the flow pattern, while the resultant chemical corrosion causes the damage.

An example of this type of attack is erosion-corrosion of brass tubes in boiler reheaters. The attack takes place where the direction of flow changes. Overheating and local boiling takes place with a disruptive effect on protective films, particularly at the exit and the entry, where turbulence is the greatest.

7.14.3.3 Postboiler Corrosion Phenomena

The postboiler system is broken down into two areas, the superheater, and the condensation and return system. Each will be considered separately:

Superheater. The allocation of the superheater to the postboiler group rather than to the boiler itself is purely arbitrary. Problems in the superheater are somewhat similar to both those of the boiler and those of the return and condensate system. For that reason it serves as an effective transition problem between the two. The attack on superheater tubes can be attributed to three corrosive factors:

1. The reaction between steam and metal at high temperatures.
2. The carryover by steam of salts that are then deposited on the metal surfaces.
3. Condensation that occurs when the system is banked or is temporarily out of service.

Corrosion of metal by steam at very high temperatures is a serious problem, but it is not amenable to solution by use of corrosion inhibitors, so it is beyond the scope of this book. It must be minimized by the choice of suitable alloying materials.

Steam condensate and return systems. Corrosion of steam condensate and return systems presents a twofold problem to power-generating and steam-heating plants. Equipment damage and frequent replacement of lines, valves, and traps result in a serious maintenance problem. In addition, corrosion products frequently formed are carried back into the steam-generating equipment and deposited there. The result is plugging of lines, localized overheating, and promotion of corrosion in the boiler system itself.

Corrosion in the condensate system manifests itself in certain typical forms, depending upon the corrosive factors involved. These factors are basically oxygen, carbon dioxide, and condensed water. Attack due to dissolved oxygen is characterized by tuberculation, pitting, and build-up of iron oxide deposits.

Oxygen concentrations below 0.5 ppm cause negligible corrosion when the temperature is less than 70 °C and the pH of the condensate is 6 or higher. In the pH range 6 to 8 and at oxygen concentrations of 0.5 to 4 ppm, the rate of attack for general corrosion is given by the equation:

$$R = 24(C - 0.4)^{0.9} \tag{7.1}$$

where R is the average rate of penetration in $mg/dm^2/day$ (mdd) and C is the oxygen concentration in ppm.

This equation is not valid for pitting corrosion and does not take into account the accelerating effect of temperature. An increase in temperature from 60 to 90 °C will double the rate of oxygen corrosion. Normally, one would expect a dual effect due to oxygen as a function of increasing temperature. On one hand, the corrosion rate should increase rapidly with temperature in accordance with normal kinetic considerations, while on the other hand, the decreasing solubility of oxygen with temperature should decrease the attack. In this particular closed system, however, the oxygen cannot escape and consequently the normal increase in reaction rate with temperature is to be expected and does in fact occur.

Carbon dioxide attack manifests itself by thinning and grooving of the metal walls with failure occurring most readily at threaded connections. The walls are relatively clean, in contrast to the masses of corrosion products that cover areas of oxygen attack. The corrosion rate of carbon dioxide is given by the equation:

$$R = 5.7W^{0.6} \tag{7.2}$$

where R is the rate in mdd and W is the concentration of carbon dioxide in the condensate in ppm multiplied by 0.1.

An increase in temperature from 60 to 90 °C raises the rate of attack of carbonic acid on low-carbon steel by a factor of 2.6. The absolute magnitude of the corrosion will, of course, vary from system

to system. A system may be found where the corrosion rate of steel panels in the desuperheating condensate system is as high as 1285 mdd prior to treatment.

7.14.3.4 Corrosion Control in Boiler Systems

Corrosion of boiler systems will be controlled by water treatment externally or internally, or both, as required. The term external treatment (pretreatment) is usually applied to clarification, softening, or demineralizing equipment, whereas the term internal treatment usually refers to treatment injected into the deaerator, feedlines, boiler, or steam condensate systems.

Preboiler treatment. Pretreatment (external treatment) is generally intended to solve both corrosion and scale problems in preboiler and boiler systems. Pretreatment of feedwater is designed to render it as non-corrosive or non-scale-forming as possible. Corrosion-control methods include various ion-exchange techniques designed to remove dissolved ionized solids from fresh water that is blended with the condensate makeup to compose the feed-water. The ion-exchange materials most commonly used for this purpose are synthetic organic exchangers, rather than the naturally occurring zeolites or their synthetic analogs, which at one time were in wide use.

Cation-exchange resins can be used to soften water by removing the hardness ions, i.e., $Ca^{2}+$ or Mg^{2+} and replacing them with sodium. Similarly, use of a cation resin in the hydrogen form produces an acid. Passage of the produced acid through an anion-resin bed in the hydroxide form results in pure demineralized water. This process can be carried out either by having one resin bed immediately after the other or by mixing the two resin types in one column. Similarly, alkalinity content and type of feed water can be controlled by a suitable exchange of ions.

Deaeration to remove oxygen from feed water must be provided if oxygen corrosion is to be avoided. Deaeration is generally accomplished through a combination of mechanical and chemical means, the most effective and economical available. A number of different mechanical systems, wherein water is heated to drive out dissolved gases, have been devised for this purpose. Oxygen removal down to $0.03\,cm^3/L$ (21 ppb) is common when the unit is operated at saturated conditions, although some units are designed to remove more oxygen.

7.14.3.5 Corrosion Control Practices

General corrosion is frequently prevented by pH control. Maintenance of pH 9.0 reduces general corrosion appreciably. There are two approaches to raising feed-water pH to this value. The earlier one consisted of either adding NaOH or recirculating alkaline boiler water and aimed at the protection of all metals generally found in these systems.

The mechanism of inhibition is as follows:

As the ($OH-$) activity is raised, the solubility of all oxides and hydroxides is reduced and the degree of supersaturation in the liquid closest to the metal is raised. This situation favors production of closely spaced nuclei of ferrous hydroxide, ferrous oxide, or magnetite, and promotes the formation of a protective film. Ferrous oxide or hydroxide are formed initially, and their transformation to magnetite can take place readily if nickel or copper are present as catalysts.

There are some inherent disadvantages to this approach, however. Sufficient recirculation of the alkaline boiler water may be impractical, or may lead to deposit problems as precipitate formation proceeds with the lowering of temperature. Use of NaOH can cause increased blowdown requirements in the boiler system. In this regard it should be noted that alkalinity arising from massive dissolution of iron is no substitute for the addition of alkali.

A more recent approach to pH control in preboiler systems involves the use of ammonia or other amines. This is necessary in systems operating above the 61 to 82 bar (900 to 1200 psig) range with high-purity water. These weak bases permit a more closely controlled regulation of pH. The following values in ppm of material are necessary to give pure water a pH of 9.0:

- Ammonia less than 0.5
- Cyclohexylamine 2.0
- Morpholine 4.0.

The use of ammonia or amines for pH control is satisfactory, provided the $O_2$and CO_2content is kept at a minimum. The primary problem appears to be oxygen and it is generally believed that use of ammonia or amines for pH control is satisfactory provided the oxygen content is carefully controlled also. Control of dissolved oxygen in the boiler water is accomplished chemically by the use of either sodium sulfite (preferably catalyzed) or hydrazine.

The level to which it is necessary to remove the dissolved oxygen to prevent corrosion varies as a function of temperature. The following are the recommended levels cited: 0.30 ppm of oxygen in cold water, 0.10 ppm in hot water (70 °C), 0.03 ppm in low-pressure boilers under 17 bars (250 psi) without economizers, and less than 0.005 ppm in high-pressure boilers or when economizers are used. It is emphasized to keep oxygen concentration at zero regardless of the system.

Sodium sulfite is used alone or as a catalyzed formulation. The catalysts ordinarily used are very small amounts of copper or cobalt. At very high temperatures sulfite alone is effective in removing oxygen from water rapidly. Varying amounts are recommended. Usually about 8 kg of sodium sulfite is required to remove 2.2 kg of oxygen. An excess of about 30 ppm of Na_2CO_3 is needed to ensure complete oxygen removal. Typical dosage values recommended by suppliers for scavenging oxygen are 20 to 40 ppm excess. Tash and Klein recommend 100 to 140 ppm Na_2SO_3 for high-pressure boiler-water composition. For a 115 bar (1700 psi) boiler, both vacuum and pressure variation is needed to reduce dissolved oxygen in the feed-water to 0.005 ppm. Catalyzed sulfite is used in the same range as uncatalyzed sulfite, but is more rapid and more effective. Activated carbon, as an additive to sulfite, functions by adsorption and concentration of the oxygen. An increase in temperature is advantageous.

Certain disadvantages are implicit in the use of sodium sulfite. One is that it can decompose to form SO_2or H_2Sin high-pressure, steam-generating equipment, thus appreciably increasing corrosion rates in the steam-fed water cycle. It is believed that limiting concentration to 10 ppm, sulfite decomposition occurs in 61 bars (900 psi) boilers. Another disadvantage is increased total dissolved solids in the boiler water, which requires more blowdown.

The catalysts can plate out in boiler tubes and promote pitting. For these reasons, there has been considerable interest in another chemical additive for deoxygenation, hydrazine (Na_2H_4). The reaction is as follows:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \tag{7.3}$$

The reaction rate of hydrazine with oxygen increases rapidly with temperature to the extent that oxygen can be substantially removed at 200 °C (400 °F) with reasonable values of reaction time and N_2H_4 concentration. At feed-water temperatures normally encountered in most industrial boiler systems, 105 to 115 °C (220 to 235 °F), the reaction rate of hydrazine is considerably slower than the sulfite-dissolved oxygen reaction rate.

A competing reaction that can cause the formation of undesirable products is the catalytic or thermal decomposition of hydrazine. The resulting ammonia may attack non-ferrous metals. Decomposition reaction of hydrazine is as follows:

$$2N_2H_4 \rightarrow H_2 + H_2 + 2NH_3 \tag{7.4}$$

and at pH 8 the reaction is:

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \tag{7.5}$$

If the residual hydrazine content of the boiler is kept below 0.2 ppm, the NH_3 content of the steam will not be greater than 0.3 to 0.5 ppm. In actual plant operation, feeding hydrazine at three to five times the theoretical amount is required to react with the dissolved oxygen left as residue in the boiler water and a produced NH_3 content in the feed water of 0.05 to 0.15 ppm. Addition of hydrazine 100%

in excess of the oxygen requirement results in a rapid rise in NH_3 and pH values, with a resultant corrosion of copper-nickel and brass tubes.

If the concentration of hydrazine is observed carefully, to prevent breakdown of the excess to ammonia, its use instead of sodium sulfite has a number of advantages. Salt content does not increase as it does when sulfite is added. Another advantage is that alkalinity can be controlled with a proper excess of hydrazine. Maintenance of a hydrazine residual in the water protects the boiler against occasional increases in dissolved oxygen content that result from variations in operating conditions. Finally, much smaller dosage levels are required.

Although sodium sulfite is more reactive than hydrazine, the latter is advantageous when air is admitted accidentally. Vapor pH is less than 7 with sodium sulfite compared to a desirable value of 9 for hydrazine. The amount of dissolved Fe decreases with hydrazine, but the amount of Cu in solution is unaffected. Hydrazine is superior economically, despite higher initial chemical cost.

Hydrazine is more efficient than sodium sulfite, and is also effective in high-pressure boilers. It is now being used in boilers with a wide spectrum of pressures, ranging from 27 to 134 bar, and is easy to apply and control.

7.14.3.6 Deposits

As indicated earlier, deposit problems in preboiler systems can be divided into two categories, based upon their origin. The first is deposition of suspended solids, which may be carried into the system with the makeup water, while the second is from dissolved solids such as calcium, magnesium, or iron.

The first problem, deposition of suspended solids, is attacked by filtration and/or clarification of the makeup water. Filters can be either gravity or pressure types. Pressure filters are usually favored in industrial plants because of their relatively small space requirements. Filtration without clarification (coagulation and sedimentation) will commonly remove only the largest particles of the suspended solids and, therefore, often will prove unsatisfactory.

Coagulation for suspended solids removal is not practiced alone as a rule, because floc can be carried over from time to time. Therefore, coagulation equipment is almost always followed by filtration. The problem of floc carryover frequently can be resolved by closer attention to operating practices, redesign of the clarification system so that more residence time is provided for the floc to settle out, or changing the chemical coagulation procedure.

Efficient operation of the coagulation and/or softening process is essential for proper feedwater maintenance. There are some high molecular weight polymeric materials that markedly improve clarification procedures.

Polymers used in the clarification process are generally required at low feed rates, usually in the range 1 to 20 ppm. Their function is to agglomerate particles that otherwise would remain small (and become floc carryover) into larger particles heavy enough to settle out of the water. The three broad classes of these polymers are:

- Cationic
- Anionic
- Non-ionic.

The effectiveness of each varies, depending upon the charge on the suspended solids and the molecular weight of the polymer. Further, some of the polymers may be used for primary or secondary coagulation. Some are of such high efficiency that they may be used just prior to a filter without the installation of clarification equipment. This latter application is referred to as “in-line” clarification.

Polyphosphates added to feed lines for deposit control also function as corrosion inhibitors. The mechanism of protection is described elsewhere in this book, in connection with cooling-water corrosion control. Polyphosphates also can prevent precipitation of hydrous ferric oxide if the water contains soluble iron.

The injection of ortho- or polyphosphate into feed water in a preboiler system that contains an economizer will invariably lead to serious economizer deposits when calcium is present. The physical condition of flow rates and water–metal interface temperatures, combined with the usual chemical environment will result in deposits that will be predominately tricalcium phosphate.

Economizer deposits are commonly composed of tricalcium phosphate, magnesium silicate, and iron oxide. Until recently, the preferred method to reduce deposits was to eliminate phosphates from the preboiler system and add organic dispersants. These dispersants include tannins and lignins, as well as synthetic polymers. While the use of organic dispersants reduces economizer deposit problems considerably, they are not the preferred treatment method. True deposit control in economizers (and preboiler systems in general) can be achieved by application of chelants to boiler systems. Chelants solubilize polyvalent metallic ions such as calcium, magnesium, iron etc. In the chelated form, such ions will not drop out of solution.

7.14.3.7 Treatment of Boilers

Deposits. The term internal treatment is used for the direct addition of chemicals to the boiler, in contrast to external treatment, which refers to mechanical processes (coagulation, softening, etc.) treating makeup water prior to the its entrance into the preboiler system. Internal treatment for prevention of deposits can be divided into two techniques, precipitating treatment, and solubilizing treatment. Each control method will be reviewed separately.

Precipitation treatments should be used for boiler pressures up to 61 to 68 bars (900 to 1000 psig). The two common techniques use phosphate control or carbonate control. These treatments involve the formation principally of calcium phosphates or carbonate sludges, their dispersion by various organic chemicals, and, finally, their removal by blowdown.

Sufficient alkalinity must be used with phosphate control because at low alkalinity values calcium phosphate becomes more soluble and tends to form a sticky adherent sludge. Adequate alkalinity for complete reaction with calcium requires a minimum pH of 9.6 in a steaming boiler, a figure comparable to 10.5 at room temperature.

The "phenolphthalein alkalinity" must be greater than one half of the "methyl orange alkalinity" and the latter value should be at least 200 ppm. A pH of 11.0 to 11.5 is favored for scale prevention and can be maintained by use of NaOH or Na_3PO_4. It must be recognized, however, that while this is a very desirable range, all makeup water does not have the same characteristics. Frequently, where external treatment has not been provided, it is necessary or desirable because of economics to operate with much higher phenolphthalein and methyl orange alkalinities, resulting in much higher boiler water pH values.

Since the mechanism involved here is one of actually reacting with the calcium on a stoichiometric basis, it is apparent that an excess of phosphate must be maintained. This excess will vary from 10 to 100 ppm of phosphate, depending on the plant operating conditions and the efficiency of the feed-water hardness control.

Because many feed-waters contain magnesium in addition to calcium, it is necessary to consider the proper internal treatment of this feed-water component. A upper limit of 100 ppm for phosphate excess is used because above this value magnesium phosphate can begin to precipitate. Magnesium phosphate deposition has been encountered even at lower phosphate values.

This is an undesirable precipitate since it is very adherent to boiler surfaces. Additionally, it will tend to cause greater volumes of hydroxyapatite and other precipitates to deposit on the boiler surfaces because of its adherent characteristics. Therefore, precipitation of magnesium in this form is to be avoided. This can be accomplished by maintaining the proper silica and hydroxide concentrations. Many feed waters do not contain sufficient silica to react with most or all of the magnesium to form the magnesium silicate precipitate identified as serpentine ($3MgO.2SiO_2.2H_2O$), and some will precipitate as the hydroxide. While both are desirable, internal conditions frequently can be

dramatically improved by adding sufficient silica as an internal treatment to precipitate the magnesium as serpentine.

Carbonate control is not practiced as widely as phosphate control. Not only is the calcium carbonate precipitate more difficult to control (i.e. remove from the boiler), but an excessive amount of soda ash must be fed to maintain an adequate amount of carbonate.

Iron or copper may be present in the feed water in an ionic form, or may be present as a metal oxide. With precipitating-type treatments, regardless of the original state, iron and copper will end up as a precipitate and increase the amount of sludge. After formation of these precipitates, whether they be phosphates, carbonates, silicates, hydroxides, or metal oxides, they must be conditioned so that they remain suspended in the boiler water as free-flowing sludge.

Unconditioned or improperly conditioned sludges tend to collect in locations where circulation rates are low and form packed layers of deposit on metal surfaces, which can interfere with circulation and heat transfer. Use of organic dispersants can help to keep this sludge in the free-flowing state.

Organic dispersing agents function not only by dispersing the sludge, but also by adsorption and crystal distortion. Crystal distortion is very important because it lessens the possibility that large crystals will form during the precipitation process and thus limits the potential for the development of a dense sludge deposit. Further, adsorption of the precipitates provides for a fluid sludge that is less adherent to boiler internal surfaces. Finally, their dispersing characteristics tend to keep the precipitates in a finely divided state, in which form they are readily removed from the boiler by blowdown.

The materials commonly used do not promote foaming and are not corrosive. The organic materials usually used for this purpose are alkaline tannin extracts, vegetable derivatives, polymeric compounds containing adjacent carboxy groups, such as a methylstyrenemaleic anhydride copolymer, carboxymethylcellulose, polyacrylates, *o*-nitrophenol dimers, colloidal peat, and a wood–fat–molasses–coal mixture.

Control of magnetic iron oxide deposits can be achieved by using sodium nitrite or an organic nitrite derivative to convert it to ferric oxide. Water-soluble lignins are more efficient in preventing Fe precipitation from water supplies than molecularly dehydrated phosphates.

Solubilizing treatments. Many problems still exist with the precipitating-type treatment programs previously outlined, even where the guidelines set forth are closely followed. Some boilers are very demanding with respect to feed-water quality and the amount of suspended solids that they will tolerate. Steaming rates per square meter of space occupied are very high in these boilers. This then correctly implies that heat transfer rates are also high, which in turn, requires improved treatment programs and leads to the common use of solubilizing treatments employing chelants. The word chelate is coined from the Greek word “chela” which means the nipper-like organ or claw terminating the limbs of certain crustaceans such as the lobster.

Thus, the word chelate is used to describe the grip of a class of amines and organic acids on metal ions, while the word chelation describes the reaction between these materials and the metal ions. Deposit control with chelants involves the use of this class of chemicals to react with metallic ions in the feed water or boiler water. The resultant chelant–metal ion complex is soluble.

Many chelating agents are available commercially. The two that have come into common use for boiler deposit control are ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). In practice, the tetrasodium salt of EDTA and the trisodium salt of NTA are used, rather than the acid. Both of these materials chelate bivalent and trivalent metallic ions on a mole for mole basis. The reaction rates for technical grades of EDTA and NTA are listed in Table 7.3.

The choice between these two chelants will depend upon many factors, such as concentration of the various metallic ions to be chelated, the concentration of chelant that can be employed economically, the degree of reactivity required in the particular application, and the chemical characteristics of the boiler water. The chelation reaction, while very energetic, is reversible under some conditions. Where high alkalinities are encountered or the feed water contains phosphate, there is competition between the dihydroxide and/or phosphate and the chelant for the metal ion.

Table 7.3 *Reaction rates of technical grades of two chelates*

Metal ions	ppm/ppm metal ion	
	EDTA	NTA
Calcium	4.67	2.75
Magnesium	4.67	2.75
Iron	8.35	4.9
Copper	7.35	4.3
Aluminum	17.3	10

This may cause some precipitation in the boiler that might not be expected otherwise. A case in point is the chelation of ion. If boiler alkalinities are allowed to over-concentrate, the high hydroxide levels may cause the iron to precipitate. This can result in iron deposits. Since EDTA is a stronger chelant than NTA, this problem is more likely to occur in an NTA-treated system.

Because chelants are organic compounds, consideration must be given to the temperature and pressure stability of these treatment materials. It has been reported that NTA should not be used in excess of 61 bar (900 psig), while the upper pressure level for EDTA is about 82 bar (1200 psig). Corrosivity of both EDTA- and NTA-treated boiler water have been investigated, with the conclusion that both materials are no more corrosive than phosphates in properly controlled boiler applications.

The solubilization characteristics of both EDTA and NTA, particularly the former, have been used to remove boiler deposits. The chelant is fed into the system at a concentration in excess of that required to chelate the metal ions in the feed water. The excess chelant will enter the boiler and react with deposits such as tricalcium phosphates and magnesium hydroxide. The calcium and magnesium will be chelated or solubilized. The sodium phosphate and sodium hydroxide, also formed, are soluble and all may then be removed by boiler blowdown.

As is the case with precipitating-type treatments, dispersants and polymeric materials are employed with the chelants. As previously pointed out, competing ions, such as hydroxides and phosphates may cause precipitation to occur to some degree in the presence of the chelant. In such cases, the polymer is used to insure that precipitate deposition will be held to a minimum.

Treatment for carryover. Carryover of boiler water with steam is first minimized by proper boiler design. Close attention to operating practices, including restricting load swings, carrying proper water level, etc. should be the second approach to reduce susceptibility to carryover problems. The last approach to be considered, is be the use of anti-foams. When the application of anti-foams is the only solution to problem attention is drown to the synthetic products. There are two major classes of anti-foam used in boiler waters – polyamide and polyoxy anti-foams.

A number of excellent polyamides are made from polyamines and carboxylic acids. For any given amine there will be a limited range of carbon atoms in the carboxylic acid for maximum effectiveness. Similarly, for a given acid the range of amines is limited. The most effective diamides can be made from ethylenediamine or diethylenetriamine and the most effective triamides from diethylenetriamine and the distearoyl amides of dibasic acids and of alkylenediamines.

Selective ion vaporization or carryover also can be a severe problem. Silica deposits on turbine blades are a frequent problem because of this selective characteristic. Severe problems have also been experienced with aluminum deposits. Such selective carryover is attacked by removing the ions from the makeup or feed water, or in some cases, by limiting concentrations in the boiler water. Boiler water silica concentration is usually regulated to assure less than 0.02 ppm silica in the steam.

7.14.3.8 Corrosion Reactions in the Boiler

The way to prevent corrosion in boilers is to keep oxygen out, maintain proper alkalinity, and keep the surfaces clean. The problem of pitting is directly associated with the presence of dissolved oxygen

and the development of deposits. The use of hydrazine or sodium sulfite, together with the prevention of scaling are optimum means of minimizing this type of attack. The other corrosive agent, copper deposition, must be prevented by proper treatment of the feed and return lines. It should be noted that oxygen can enter the system by leakage, so it is essential to ensure that an excess of sodium sulfite or hydrazine is present in the boiler. One method of is to add some of the oxygen scavenger directly to the boiler on a continuous basis.

The problem of corrosion, because of high localized NaOH concentrations, is generally attacked by one of a number of methods, all of which rely on proper ratios of various salts and alkalinity in the boiler water. Thus, the need for close control of boiler-water composition and frequent analysis to verify the control becomes apparent. The pH control situation is very complicated because, while the hydroxyl ion will passive the surface, too much will cause cracking. The problem then is to use a system that substitutes something else for most or all of the NaOH as a source of alkalinity. The coordinated pH approach rests upon the premise that the alkaline pH should come from trisodium phosphates as much as possible, rather than from NaOH.

Corrosion and scale formation in low-pressure boilers can be held to a minimum by maintaining the boiler water at a hydroxide alkalinity of 100 to 350 ppm and a total alkalinity of 300 to 500 ppm, both expressed as $CaCO_3$.Addition of silicates, carbonates, phosphates, and chromates can make up the non-hydroxide alkalinities. In this case alkalinities up to 1000 ppm do no harm.

Corrosion of boilers operating below 14 bar (200 psi) can be controlled by keeping total alkalinity at 10 to 15% of the total dissolved solids. When the boilers go over this pressure, deoxygenation of water is helpful. Alkaline phosphates can protect boiler steels subjected to a substantial amount of stress and the combined action of caustic soda and silica, providing the ratio of Na_3PO4 to NaOH is equal to or greater than one to prevent caustic cracking. In drum-type boilers without stages of evaporation, the excess PO_4^{3-} concentration should be maintained below 40 ppm and NaOH alkalinity at 9 ppm, minimum. For boilers with stages of evaporation, the last stage should show a maximum of 100 ppm PO_4^{3-} and a minimum in the boiler of 5 to 7 ppm, with the water tinged by phenolphthalein.

A ratio of Na_3PO_4 to NaOH equal to or greater than one is necessary to prevent cracking. Phosphated waters that produce cracking may invariably have more NaOH than PO_4^{3-}. It should be noted that the use of the Na_3PO_4 to NaOH ratio is not certain and Na_3PO_4 functions well in the absence of hydroxide ions, a situation that occurs only infrequently in boilers.

Another approach to the prevention of caustic cracking involves maintenance above a certain value of the ratio of sodium sulfate to alkalinity in the boiler water. If chemically treated water is used along with condensate as the feed water, then the ratio of Cl^- plus SO_4^{2-} to NaOH should be no less than five. Excessive alkalinity may be reduced by neutralizing with H_2SO_4 and then using an ion-exchange resin to free the water of excess alkalinity by replacing Na^+ ions with H^+ ions. The most widely accepted chemicals for the prevention of caustic embrittlement are the nitrate ion and quebracho extract. The amount of nitrate used is critical and must be 35 to 40% of the total alkalinity, calculated as NaOH.

The US Bureau of Mines recommends using ratios dependent on boiler operating pressure, as given in Table 7.4. Potassium nitrate functions as well as the sodium salt and waste sulfite liquors containing

Table 7.4 *US Bureau of Mines ratios of sodium nitrate/sodium hydroxide to boiler pressure*

Pressure, bar	Ratio of $NaNO_3$:NaOH
Up to 17	0.2
Up to 27	0.25
Up to 48	0.4

$NaNO_3$ are also effective. Tannins and butyric acid (in the amount of 0.5% of the amount of alkali present) are also effective in preventing caustic embrittlement.

For preventing chloride stress corrosion attack on austenitic stainless-steel-tubed steam generators, nitrate and sodium sulfite are effective inhibitors. The combination of the two is superior to either inhibitor alone or to any other inhibitor or combination. These inhibitors are effective in alkaline phosphate boiler water containing up to 500 ppm chloride.

The erosion-corrosion problem in boiler tubes is addressed by:

- redesigning the system to avoid turbulent flow,
- eliminating deposits and keeping the tubes clean,
- preventing corrosion of the copper in the preboiler and postboiler systems,
- maintaining proper dosage of the corrosion inhibitors previously mentioned, especially the oxygen scavengers.

The solution thus becomes a combination physical and chemical approach.

7.14.3.9 Control of Postboiler Corrosion

Superheater. It was pointed out earlier that the corrosion of metal by steam at very high temperatures is not readily prevented by the use of corrosion inhibitors. The most satisfactory preventive technique involves the choice of suitable alloys, a procedure beyond the scope of this book.

Carryover of salts by steam is best attacked by preventing carryover. This is usually accomplished in the boiler by using properly designed steam separators and anti-foaming agents. Corrosion due to condensation of steam in superheaters is treated in the same manner as corrosion of steam condensate and return systems.

Steam condensate and return systems. The causes of corrosion in the steam condensate and return systems are oxygen and carbon dioxide. The development of corrosion inhibitors for these systems should therefore bear these two factors in mind. The first problem, corrosion due to oxygen, is generally solved by the techniques described for eliminating the oxygen content of boiler water. This method usually insures that oxygen present in condensate will be derived essentially from leaks in the return systems. When oxygen leakage into the return system becomes sufficient to promote corrosion, then the preferred solution is mechanical, designed to eliminate the leaks, or else metallurgical, calling for the use of proper alloys. Sodium sulfite can be added to the condensate system when oxygen cannot be eliminated in any other manner. A preferred approach is to increase condensate pH with volatile amines. Raising the pH of the condensate will minimize oxygen attack.

A very successful approach to the problem of acidic corrosion caused by carbon dioxide involves using volatile amines. They are added to the boiler water, volatilize along with the steam, condense with it, neutralize the carbon dioxide and produce a condensate having a neutral or alkaline pH. Alternatively, they can be added to the steam lines. In either event, they stay with the steam, thus providing alkaline material at the places it is needed.

A number of amines have been employed for this purpose. The most obvious one is ammonia. The material is generally added to the boiler feed water as ammonium hydroxide or ammonium sulfate, with the resultant liberation of ammonia in the boiler. The major use of ammonia is in central stations with low percentage makeup and low carbon dioxide concentrations in the steam. When carbon dioxide concentrations are quite high, as they tend to be in industrial plants, the required ammonia level for neutralization becomes high, and this treatment runs into the disadvantage of serious corrosion of copper- and zinc-bearing metals. For this reason, other neutralizing amines have been developed that are not corrosive to copper at the dosages required for carbon dioxide neutralization.

The two neutralizing amines used most frequently are morpholine (C_4H_9NO) and cyclohexylamine ($C_6H_{11}NH_2$). Both chemicals are being sold in considerable quantities under different trade names by inhibitor manufacturers.

At 25°C, the pH at which carbonic acid is completely converted to morpholine bicarbonate is slightly higher than 7.3, but it should be noted that contamination of the condensate by 1% of a synthetic boiler water raised the pH from 7.3 to 8.0 and lowered the untreated corrosion rate. Due to this phenomenon, plants having trouble with boiler-water carryover in the steam usually do not have condensate corrosion problems as serious as those where there is no carryover. Morpholine is stable at high temperatures and pressures and is evenly distributed. For effective corrosion control, a pH of 8.8 to 9.0 and a morpholine residual of 3 to 4 ppm are maintained. Morpholine is stable up to a boiler pressure of 170 bar (2500 psi) and to 650 °C (1200 °F) in superheated steam.

Cyclohexylamine and dicyclohexylamine as inhibitors can prevent the corrosion of iron by steam condensate containing oxygen and carbon dioxide. Several other volatile amines, such as benzylamine, 2-diethylaminoethanol, ethylene diamine, and amino alcohols are also effective.

The concentration of an amine at any location in a steam-condensate system is dependent on the distribution ratio. This ratio is a comparison of the amount of amine in the steam with the amount present in the condensate. The ratio for cyclohexylamine is three, whereas that for morpholine is only 0.4. This would indicate that a greater concentration of morpholine will be found in the condensate. This characteristic makes it well suited for applications in central stations where protection is required at the wet end of high-pressure turbines. The relatively high distribution ratio of cyclohexylamine makes it more applicable in the extensive steam-condensate systems found in refineries and petrochemical plants.

The differing distribution ratios of the volatile amines have been used in commercial return- line corrosion inhibitors. These inhibitors are generally combinations of morpholine and cyclohexylamine blended so as to obtain the benefits of the differing distribution ratios. Amine requirements are approximately 3.6 ppm morpholine (40%) or 3.0 ppm cyclohexylamine (40%) per ppm of carbon dioxide to elevate the condensate pH to 7.0.

The volatile amines can be added to the steam condensate system by addition to the feed-water, boiler, or return lines, but there are some advantages and disadvantages for each approach. Some prefer direct addition to the boiler or else the feed water. One objection to this method is that it becomes necessary to treat the entire system to obtain adequate protection in a desired localized section. In the latter case, the preferred method is direct injection of the inhibitor into the steam or condensate lines, by means of a chemical feed pump.

Another approach to the prevention of steam condensate and return line corrosion is that of using "film-forming" chemicals to lay down a protective film on surfaces. This approach has come into widespread use with the development of suitable long-chain nitrogenous materials for this purpose. It is especially effective in systems where high concentrations of carbon dioxide make the use of neutralizing amines uneconomical.

One approach involves film-forming materials, such as sodium silicate, oils, or polyphosphates. Sodium silicate reduces corrosion but cannot prevent it entirely. A very successful approach is the use of long-chain nitrogenous compounds as film formers for condensate and return lines. They do not normally accumulate in the boiler because they are either eliminated at the vent of the deaerating heater or steam distil from the boiler water.

While a number of materials are now being employed, octadecylamine ($C_{18}H_{37}NH_2$) and its salts are most frequently used, and typify this class. The film-forming inhibitors, as well as the emulsifying or dispersing materials that may be used with them, have strong surface active properties. Consequently, their introduction into the system can result in the loosening of previously formed deposits and hence clogging of the lines by these materials.

For that reason it may be better to clean the lines before starting to use the inhibitor, or alternately to clean out the system after the loosened deposits have begun to accumulate. This cleaning will improve heat transfer, as well as corrosion inhibition.

The use of film-forming inhibitors becomes economical when the carbon dioxide content of the steam is so high that the cost of using sufficient neutralizing amine is excessive. By contrast, the

dosage of filming amines is independent of dissolved gas concentration. Typical dosage is 0.5 to 10 ppm, with 2 ppm as the recommended level. On the other hand, levels of 15 to 30 ppm of a commercial dispersed filming amine, to establish and maintain the desired corrosion resistant film on the metal surfaces, are recommended. By using a treatment level of 3 to 4 ppm of octadecylamine, satisfactory inhibition of the distribution system of a large process steam plant caused by 2 ppm oxygen and 4 to 5 ppm carbon dioxide in the condensate and makeup can be achieved. Interruption of treatment for a few hours can be tolerated because of the film that has been built up.

The rate at which the protective film builds up is quite important. The effectiveness of the inhibitor is also a function of time and the corrosion rate decreases gradually if sufficient amount of inhibitor is not used. For this reason the film-forming inhibitors can be classified as "dangerous." If enough inhibitor to form a continuous film is not used, then anodic action leading to severe local attack can occur. It is desirable to start treatment at a high dosage level to lay down the protective film rapidly and then to reduce the treatment level to that necessary to maintain and repair the film.

There is some disagreement as to the desirable feeding point for film-forming inhibitors. All inhibitor suppliers say that the materials can be fed directly to the steam and condensate systems. Some suppliers recommend adding the inhibitor to the feed water or directly to the boiler and say that the inhibitor will evaporate with the steam and condensate in a thin, continuous film. However, most of the commercially available filming inhibitors are formulated products, each component having a somewhat different volatility (and solubility) and, therefore, the preferred point of addition should be the steam header.

In some cases, the use of filming amines has led to deposit formation, particularly following the use of the first developed inhibitor, octadecylamine acetate. These deposits were polymerized amine and oil–oxide combinations. It was originally thought that over-feeding of the inhibitor was the only cause of these accumulations, but investigation led to the conclusion that the octadecylamine acetate had polymerized with iron oxide and/or oxygen. Improved formulations were developed to eliminate this problem. Current commercial inhibitors have stabilizing agents that hinder polymerization and thus deposit formation.

7.14.4 High-temperature hot water systems

A high-temperature hot water system is usually defined as a system operating above 149 °C (300 °F). The corrosion problems associated with such systems are summarized below:

- Acidity (low pH due to carbon dioxide and/or decomposition of organic matter)
- Dissolved gases (primarily oxygen)
- Galvanic action (due to contacts among dissimilar metals).

In a properly designed system there is little opportunity for scale formation, because there is no evaporation within the system and thus little makeup water is needed. Therefore, solids in makeup water do not concentrate, and saturation values are not exceeded. However, when designing such a system, it is a good practice to include the use of a pretreatment, such as zeolite softening.

Demineralized water also may be used sometimes as makeup. Characteristics of makeup water are important with respect to corrosion in high-temperature hot-water systems. If the circulating water pH is properly adjusted, much of the corrosion potential can be minimized. In all-steel systems, the pH can be adjusted to 11.0 to minimize corrosion. However, in bimetallic systems, pH values should not be allowed to reach this level because of possible alkaline reaction with brass, bronze, copper, and/or aluminum.

Before a new hot water system is put into operation, it should be cleaned of all pipe dope, grease or cutting oils, dirt, sand, and soldering flux. If these substances are not removed, they may result in the formation of concentration cells and greatly increase the corrosion load. Phosphates are

most commonly used for cleaning. A satisfactory cleaning solution is a 2% solution of sodium hexametaphosphate or sodium tripolyphosphate.

Chromates, nitrates, nitrites, borates, and silicates have been employed as corrosion inhibitors in hot water circulating systems. However, their use must be carefully controlled because they can cause problems in mechanical or patent circulating pump seals. Evaporation can occur, resulting in crystallization of the inhibitor, with resultant wear on moving parts. Buffered chromates at 150 to 250 ppm concentration have been employed successfully.

7.15 Treatment of Acid Systems

7.15.1 Industrial Exposures of Metals to Acids

Metals are exposed to the action of acids in many different ways and for many different reasons. The exposures can be severe, but in many cases, the corrosion can and should be controlled by means of inhibitors. Processes in which acids play a very important part are:

- *Acid pickling*. In these processes, undesirable oxide coatings are removed from metals – usually ferrous metals – and the surface is prepared for further operations, such as phosphate coating, enamelling, electroplating, painting, etc. The acid of choice has for many years been sulfuric acid.
- *Industrial acid cleaning*. This very important procedure is applied chiefly to the removal of scale and other unwanted deposits from steam-generating equipment and from chemical and petrochemical reaction vessels, as well as cooling system. Hydrochloric acid is widely used, frequently with important assistance from hydrofluoric acid or fluorides.

Tests, reported by NACE, show that at 74 °C, concentrations of inhibitor at 0.03% reduced corrosion rates in 5, 10, and 20% acid from 0.1 to a little more than 0.001 $mg/cm^2/day$, rates at all three concentrations clustered about the same point. At 95 °C, under the same conditions, results were more scattered, the rate for 10% acid being reduced from 0.1 $mg/cm^2/day$ for the uninhibited control to a little less than 0.01 $mg/cm^2/day$ in 5% acid; with slightly increased corrosion rates for the 10 to 20% concentrations. Rates of all three at 95 °C were less than 0.01% for 0.03% inhibitor concentration.

7.15.2 Cleaning of Oil Refinery Equipment

The maximum temperature for inhibited hydrochloric acid used for cleaning cast iron in petroleum refinery equipment is 51°C (125 °F), while other metals can be cleaned safely at 77 °C (170 °F). Using 7.5% acid at 77 °C (170 °F) causes graphitization of some cast irons, particularly those with combined carbon.

In cleaning systems that include stainless steel, extreme care must be taken to assure that all the acid is thoroughly flushed from the system, because retained chloride ions will cause disastrous stress corrosion cracking. Copper, plating out on steel surfaces from ions dissolved from copper tubing in heat exchangers, is another hazard of circulating cleaning procedures. Copper ions react with the iron in an oxidation reduction against which most inhibitors are ineffective.

Production of explosive and poisonous gases is a hazard in acid cleaning. Hydrogen gas must be vented and precautions taken against fire and sparks. Hydrogen sulfide, hydrogen cyanide, arsine, and phosphine have been found in vessels being cleaned. Neutralization of these gases by caustic, or burning or venting to the atmosphere is necessary.

Because ferric ions accelerate corrosion by cleaning solutions, a limit of 0.4% by weight usually is the “accepted” maximum. A 1% solution of ferric ions has been known to increase the corrosion rate by a factor of nine.

Table 7.5 *Influence of inhibitors in 5% hydrochloric acid on rates of dissolution of iron oxides and sulfides*

	% Inhibition in dissolution of:					
Inhibitor	Low-carbon steel	Free machining steel	FeS	FeS_2	FeO	Fe_3O_4
C	66	71	5	–	13	170
B	98.2	99.7	50	–	38	12
A	99	99.9	23	–	62	–
D	98.5	–	15	–	75	10

Note: (–): Sign indicates slight acceleration of dissolution. In the case of Fe3O4 in inhibitor C, acceleration of dissolution as compared with plain 5% HCl was by 170%.
All tests were at 66 °C (150 °F) in 5% acid for 2 hours.

Table 7.5 shows some of the results of NACE tests using various inhibitors to reduce corrosion rates of refinery equipment from acid cleaning solutions. Stannous chloride, lead nitrate, and lead acetate were tested in an effort to reduce the accelerated corrosion that sometimes occurs in crevices; however, they were ineffective in the presence of hydrogen sulfide. Accelerated attack may also occur because of galvanic couples between metals differing in their solution potentials. Low-carbon steel was 0.031 mV positive to Type 304 steel in one test.

Spent acid from one cleaning operation should not be used in another because of possible bad effects from concentrations of cupric or ferric ions in the used solutions. All stainless steel systems can be cleaned effectively using sulfuric or nitric acid solutions. Stainless steels that have reached their sensitization temperature are likely to suffer intergranular attack.

7.15.3 Heat Exchangers

By injecting hydrochloric acid solutions of 1–2N concentration, and containing a commercial inhibitor, directly into cooling water immediately before it enters an operating heat exchanger, the exchanger can be cleaned on-stream. This procedure exposes the copper tubing to the acid for several minutes with no apparent ill effects. Scale removed by the treatment, along with residual acid, is recirculated in the system with no problems. Inhibitors are very important in chemical cleaning and their selection and use are important ingredients in a successful job.

7.15.4 Oil-Well Acidizing

For oil-well stimulation, large quantities of acid – usually hydrochloric – are pumped at high rates of flow through the oil-well tubing into the producing formation. The primary object is to act on the formation in such a way as to stimulate the oil flow. If the nature of the formation requires it, hydrofluoric acid is added to the hydrochloric acid.

Oil-well acidizing represents a severe test for inhibitors. The acid concentrations are high – usually 10 to 15% HCl by weight and at times 28%. Temperatures at the bottom of the hole can be as high as 177 °C (350 °F). Effects of agitation, exposure, time, acid type and concentration, and inhibitor concentration at 38 to 177 °C (100 to 350 °F) have been reported.

7.15.5 Manufacturing Processes

In this very broad field, very little that is specific can be said. Usually it is the intent of the manufacturer to select reaction vessels from alloys that will be resistant to reactants and products in the process. If this is not feasible, other means must be used for protection, one of which could be the use of inhibitors.

It is usually desirable to select alloys that are resistant to the acid to be stored. When this is not possible, it is necessary to protect the metal (usually mild steel) by means of a suitable inhibitor.

7.15.6 Vapor–Liquid Systems: Condensing Vapors

One of the most important examples of corrosion from condensing acid vapors is that of combustion gases, where SO_2 is converted to SO_3, which forms sulfuric acid by reacting with water condensed in the cooler zones of the combustion equipment. Attempts should be made to protect such zones by means of inhibitors.

7.16 Chemical Cleaning of Process Equipment

Process equipment and piping should be cleaned to prevent contamination of a process or product, to improve the operation of a process, to reduce the opportunity for premature failure, and to prepare equipment for inspection. However, equipment should be cleaned only for good reason. In addition to the cost of unnecessary cleaning, problems may be introduced. For example, most chemical cleaning processes cause some metal loss. In other cases, washing before cleaning may cause accelerated corrosion, such as during the preparation of a concentrated H_2SO_4 storage tank for inspection. Other potential problems are:

- Difficulties associated with pumping hot corrosive through temporary connections.
- Difficulties associated with a crowded work space, for example, during a turnaround.
- The need to dispose of waste.
- The possibility of generating toxic or flammable by-products during cleaning.

There are four types of equipment cleaning: preoperational, chemical, mechanical, and on-line. These must be evaluated for each job in order to select the most cost-effective. To make a sound evaluation, the deposit to be removed should be thoroughly characterized.

7.16.1 Fouling of Equipment

Deposits that cause fouling accumulate in equipment and piping and impede heat transfer or fluid flow, or cause product contamination. Deposits may be organic, inorganic, or a mixture of the two. Scales are crystalline deposits that precipitate in a system (see Table 7.6). There are four principal sources of deposits: water-side, fire-side, process-side, and preoperational.

7.16.1.1 Water-Side Deposits

Water-side deposits are of many types. Hardness (calcium and magnesium)-based deposits and iron oxide are the most common water-side deposits and often affect boilers and cooling systems. Process and oil leaks can foul boilers and cooling systems. Biofouling, mud, and debris are often found in cooling systems. Treatment chemicals, if not properly controlled, can add to deposits and scales. Silica can form hard, adherent deposits in boilers, steam turbines, and cooling systems. Corrosion products can add to deposits.

7.16.1.2 Fire-Side Deposits

Fire-side deposits can be extremely corrosive. Slags from burning oil and waste can corrode boiler equipment if they become moist. Fly ash deposits can accumulate in coal-fired boilers. Gas-fired boilers are generally clean. Some compounds that are burned in incinerators or waste heat boilers can seriously corrode or erode boiler tubes.

Table 7.6 *Summary of common types of scale-forming minerals*

Scale	Chemical formulas
General	
Sodium iron silicate	$NaFe(SiO_3)_2$
Barium sulfate	$BaSO_4$
Sodium aluminum silicate	$NaAlSi_2O_6.H_2O$
Aragonite (rhombic crystals)	$CaCO_3$
Calcium carbonate – (hexagonal crystal)	$CaCO_3$
Calcium sulfate	$CaSO_4$
Magnesium carbonate and hydroxide	$3MgCO_3.Mg(OH)_2.3H_2O$
Calcium phosphate	$Ca_{10}(OH)_2(PO_4)_6$
Iron oxide	α -FeO(OH)
Iron oxide (magnetite)	Fe_3O_4
Iron oxide (red)	Fe_2O_3
Iron chrome spinels	$CrFe_2O_4$
Iron sulfide	FeS
Magnesium hydroxide	$Mg(OH)_2$
Magnesium oxide	MgO
Manganese dioxide	MnO_2
Aluminum silicate	$Al_2O_3.4SiO_2.4H_2O$
Sodium aluminum silicate	$Na_8Al_6Si_6O_{24}.SO_4$
Calcium sodium silicate	$4CaO.Na_2O.6SiO_2.H_2O$
Magnesium silicate	$Mg_3Si_2O_7.2H_2O$
Silica	SiO_2
Sodium aluminum silicate	$Na_8Al_6Si_6O_{24}.Cl_2$
Magnesium iron aluminum silicate	$(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2.4H_2O$
Calcium silicate	$5CaO.5SiO_2.H_2O$
Copper or copper alloy equipment	
Copper iron sulfide	CuFeS
Copper sulfide	CuS and Cu_2S
Basic copper chloride	$CuCl_2.3Cu(OH)_2$
Copper oxide	Cu_2O
Chalcopyrite	$CuFeS_2$
Beta zinc sulfide	ZnS
Green basic carbonate	$CuCO_3Cu(OH)_2$

7.16.1.3 Process-Side Deposits

There are many types of process-side deposits. Organic residues, tars, and coke are common in the petroleum and petrochemical industries. Iron oxide and sulfides are often present in these organic deposits. Sulfate deposits are common in H_2SO_4 plants. Iron-, copper-, and nickel-containing deposits often occur in HF plants. Organic deposits may develop through the polymerization of leaking gases or from the decomposition of process constituents. In some cases, organics help to bond inorganic deposits, such as iron oxides or sulfides.

Some process-side deposits are pyrophoric when exposed to air or oxygen. The most common is iron sulfide, which is likely to be found in natural-gas and petroleum-refining processes or when aqueous solutions of hydrogen sulfide (H_2S) are dried in the absence of air.

7.16.1.4 Preoperational Deposits

Preoperational deposits are formed during the fabrication and erection of process equipment and piping. In addition to mill scale residues, metal surfaces become coated with dirt, oil, grease, weld spatter, pipe-threading compound, protective shop coatings, and corrosion products.

Highly alloyed materials, such as stainless steels, nickel-based alloys, reactive metals, or high-temperature alloys, may become contaminated with iron from tooling; zinc, cadium, and aluminium from scaffolding; and zinc, sulfur, and chlorine from certain manufacturing materials. These elements can cause corrosion or embrittlement.

7.17 Critical Equipment Areas

Requirements for cleaning will vary with the type of equipment. The operating characteristics and design should be assessed before selecting a cleaning method.

7.17.1 Columns

The two critical areas for deposit formation in a column are at the trays, where vapor passes through a valve, sieve, flapper, or riser, and in the flash zone, where vapor condenses. Operating history sometimes indicates which areas require cleaning; for example, the vapor line is suspect if the column vapor rate becomes limiting. Inspection is necessary to determine the extent and location of fouling.

7.17.2 Glass-Lined Vessels

Glass-lined vessels require special attention when their water jackets are chemically cleaned. The recommendations of the manufacturer must be followed. The most commonly recommend cleaning solution is dilute alkaline sodium hypochlorite (NaClO). If strong acids are used, atomic (nascent) hydrogen formed by corrosion diffuses into the shell and recombines as hydrogen molecules at the glass/metal interface, which causes spalling of the glass.

7.17.3 Oxygen, Chlorine, and Fluorine Piping Systems

Oxygen, chlorine, and fluorine piping systems must be free of organic contaminants. Organic materials, particularly hydrocarbon greases and oils, react violently with these chemicals.

Preoperational cleaning is mandatory in such cases. After cleaning, the lines should be blown dry, using oil-free nitrogen or air.

7.18 Identification of Deposits

To select an effective cleaning procedure, the deposit must be characterized, or identified. The sample should represent the deposit in the most critical fouling area. For exchangers and boilers, this is the highest heat transfer section. Expediency should not dictate the location of the sample. A cleaning procedure should not be based on a sample of loose deposit from a non-critical area, because the sample at this location may not be representative.

Table 7.7 *Components of boiler deposits*

Mineral	Formula	Nature of deposit	Usual location and form
Acmite	$Na_2O.Fe_2O_3.4SiO_2$	Hard, adherent	Tube scale under hydroxyapatite or serpentine
Alpha quartz	SiO_2	Hard, adherent	Turbine blades, mud drum, tube scale
Amphibole	$MgO.SiO_2$	Adherent binder	Tube scale and sludge
Analcite	$Na_2O.Al_2O_3.4SiO_2.2H_2O$	Hard, adherent	Tube scale under hydroxyapatite or serpentine
Anhydrite	$CaSO_4$	Hard, adherent	Tube scale, generating tubes
Aragonite	$CaCO_3$	Hard, adherent	Tube scale, feed lines, sludge
Brucite	$Mg(OH)_2$	Flocculent	Sludge in mud drum and water wall headers
Copper	Cu	Electroplated layer	Boiler tubes and turbine blades
Cuprite	Cu_2O	Adherent layer	Turbine blades, boiler deposits
Gypsum	$CaSO_4.2H_2O$	Hard, adherent	Tube scale, generating tubes
Hematite	Fe_2O_3	Binder	Throughout boiler
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	Flocculent	Mud drum, water walls, sludge
Magnesium phosphate	$Mg_3(PO_4)_2$	Adherent binder	Tubes, mud drum, water walls
Magnetite	Fe_3O_4	Protective film	All internal surfaces
Noselite	$4Na_2O.3Al_2O_3.6SiO_2.SO_4$	Hard, adherent	Tube scale
Pectolite	$Na_2O.4CaO.6SiO_2.H_2O$	Hard, adherent	Tube scale
Serpentine	$3MgO.2SiO_2.H_2O$	Flocculent	Sludge
Sodalite	$3Na_2O.3Al_2O_3.6SiO_2.2NaCl$	Hard, adherent	Tube scale
Xonotlite	$5CaO.5SiO_2.H_2O$	Hard, adherent	Tube scale

Table 7.7 lists some common components of boiler deposits. When removed by scraping, the samples should be as intact as possible. They should be removed to the base metal, taking care not to introduce any metallic chips from the blade or substrate.

Thickness, density, porosity, type (homogeneous or layered), and color should be noted. When only a limited amount of deposit is available, replication tape is a useful method of removing it. Polyvinyl chloride (PVC) or other chloride-containing tapes should not be used on stainless steels, which are susceptible to chloride pitting and stress cracking.

Many analytical techniques are used to characterize deposit samples. Typical methods include X-ray diffraction, optical emission spectroscopy, and X-ray spectrometry. Most chemical cleaning contractors, water treatment supplies, and analytical laboratories have the facilities to characterize deposits.

7.18.1 Preoperational Cleaning

Unlike process- or water-side deposits, the types of deposits in original equipment are easily categorized. Preoperational cleaning should include consideration of the degree of cleanliness required and the material of construction. Areas where preoperational cleaning is used include:

- Process equipment start-up, boilers, and steam-generating and compression systems
- Lubricating oil systems before oil systems
- Critical services, such as oxygen, chlorine, or flouring piping
- Water treatment and inhibition programs.

7.18.2 Boilers

Boilers are cleaned to remove oils, grease, and mill scale. When boilers are coated with heavy protective greases, two-stage cleaning (for organic and inorganic deposit removal) should be used. A degreasing step using alkaline boil-out solutions or emulsions is used first. Common second-step solvents include chelants, organic acids, or HF.

7.18.3 Columns

Columns contain similar contaminants. They are cleaned by fill and soak, cascade, or foam methods, using solvents similar to those used for boilers. The design of the column may eliminate certain methods, such as cascade cleaning for a packed column.

7.18.4 Shell and Tube Heat Exchangers

The most serious fouling is found on the interior (tube side) or exterior (shell side) of the tubes. Other locations are on the shell side at baffles or drain nozzles.

The head should be removed for inspection if tube-side fouling of the tubes is suspected. The shell is more difficult to inspect, unless the tube bundle is removable, but limited information may be gained through nozzles.

Heat-exchanger tubes may be cleaned mechanically or chemically. Mechanical cleaning may damage tubes. Individual tubes should not be steam blown, because this may damage rolled tube joints. Tubes should not be hammered with any metallic tool, and scraping or rodding should be done with care because any scoring or gouging can lead to premature failure. High-pressure and ultra-high-pressure water cleaning are preferred. Chemical cleaning methods use circulation, fill and soak, or foam. However, severely blocked tubes may resist the entry of the cleaning agent or may retain it beyond the neutralization step of the cleaning process, leading to corrosion during shut-down or in service.

Heat-exchanger shells are normally chemically cleaned using the circulation or the fill and soak method. If the tube bundle is removable, mechanical cleaning with high-pressure or ultra-high-pressure water is good practice.

7.18.5 Cleaning of Boilers

Water-side deposits found in boilers vary depending on raw water composition, feed-water treatment, and operating pressure.

The heaviest deposition occurs in tubes with the highest heat input, an area that may be physically impossible to inspect. A tube section can be taken from the area where deposition is known to be heaviest in order to characterize the deposit. Although various ways (in grams of scale per square foot) have been proposed for determining the need to clean, each case should be individually evaluated. Factors to be considered are the degree of fouling, the type of service, the reliability required, the operating history, and future operation.

Chemical cleaning of the water side is generally more effective than mechanical cleaning, particularly in designs with heavily swaged tubes and tight bends. Preoperational cleaning of boilers must be conducted to allow the steel surface to develop a protective film of magnetite (Fe_3O_4), when the boiler is put into service and to remove mill scale.

7.18.6 Cleaning of Furnaces

The external fouling of furnace tubes depends on the nature of the fuel. Oil-burning furnaces usually have significantly more deposit formation and corrosion problems than coal-burning types, while natural-gas-burning furnaces have very few problems.

Slag accumulates when metallic salts and oxides are vaporized and condense in various parts of the furnace. Because its melting point is relatively low, the slag forms a sticky corrosive deposit of various salts, primarily sodium and vanadium. These slags should be mechanically removed by chipping or dry sandblasting. Wet cleaning methods may cause acid formation. For internally cocked tubes, steam-air decoking or mechanical cleaning is preferred.

7.18.7 Cleaning of Pumps and Compressors

Cooling water jackets are often chemically cleaned to remove iron oxide, water-formed scale, and possible oil infiltration. All loose material is first removed by opening the clean-out plates and flushing. A two-stage chemical cleaning process is then used, first to dissolve any organic deposits and then to remove inorganic scales. The acidic cleaner selected for inorganic scales should be compatible with the materials of construction.

7.18.8 Cleaning of Piping

Piping may contain various contaminants, including dirt, loose paint, sand and grit, varnish, grease and oils, weld spatter, mill scale, and rust. Piping should first be inspected and all construction debris removed. Dirt, loose paint, sand, and grit are removed by flushing with clean water or blowing with dry compressed air or steam. Varnish, grease, and oils are removed by steam blasting with detergent or hot water containing an alkaline degreasing agent. Mechanical cleaning may be required, depending on the amount of weld spatter, mill scale, and rust. The piping may then be chemically cleaned if necessary, using organic acids and chelants, followed by neutralizing and passivating.

Moisture removal may be required for such specific applications as compressor or refrigeration piping. When all traces of moisture must be removed, the system can be filled with alcohol, evacuated to evaporate the alcohol, then flushed with an inert gas. Piping carrying oxygen, chlorine, and fluoride requires stringent cleaning to remove organic contamination. No organic-containing residues can be permitted.

7.19 Chemical Cleaning

Chemical cleaning is the use of chemicals to dissolve or loosen deposits from process equipment and piping. It offers several advantages over mechanical cleaning, including more uniform removal, no

need to dismantle equipment, lower overall cost (generally), and longer intervals between cleanings. In some cases, chemical cleaning is the only practical method.

The primary disadvantages of chemical cleaning are the possibility of excessive equipment corrosion and solvent disposal. Chemical cleaning solvents must be assessed in a corrosion test program before their field acceptance. Chemical cleaning is performed by a contractor who specializes in this work. Some cleaning procedures are protected by patents.

7.19.1 Chemical Cleaning Methods

There are six major chemical cleaning methods: circulation, fill and soak, cascade, foam, vapor-phase organic, and steam-injected cleaning.

7.19.1.1 Circulation Cleaning

The most common method is applied to columns, heat exchangers, cooling water jackets, and so on, where the total volume required to fill the equipment is not excessive. The equipment is arranged such that it can be filled with the cleaning solution and circulated by a pump to maintain flow through the system. Movement of solution through the equipment greatly assists the cleaning action. As cleaning progresses, temperature and concentration are measured in order to monitor the progress. The cleaner may be replenished (sweetened) occasionally to maintain efficiency. Corrosion coupons or on-line monitoring determines the effect of the cleaning chemicals on the equipment materials.

With circulation cleaning, the rate of flow through the equipment is critical. Large-diameter connections are preferred, and a high-capacity pump may be necessary to produce the required circulation. After cleaning, the equipment is drained, neutralized, flushed, and passivated.

7.19.1.2 Fill and Soak Cleaning

It involves filling the equipment with the cleaner and draining it after a set period of time. This may be repeated several times. The equipment is then water flushed to remove loose insolubles and residual chemicals.

Fill and soak cleaning offers limited circulation. The poor access of fresh cleaning solution to the metal, together with the inability to maintain solution temperature, may cause the cleaning action to cease.

This method is limited to relatively small equipment containing light amounts of highly soluble fouling, and to equipment in which circulation cannot be properly controlled. Because good agitation is achieved only during the flushing stage, flushing should be as thorough as possible. Circulation and fill and soak cleaning are sometimes used alternately.

7.19.1.3 Cascade Cleaning

This is a modification of the circulation method, usually applied to columns with trays. The column is partially filled, and the liquid is continuously drawn from the reservoir and pumped to the highest point. The liquid then cascades down through the column, cleaning surfaces as it passes over them. The liquid draw-off point must be suitably located to avoid recirculation of loosened foulants. High-capacity pumps and large-diameter piping are required to achieve the necessary transfer of liquid to produce a flow pattern that will contact all fouled surfaces within the column. The cascade method is primarily used in large columns and is suitable for most types, except for packed columns. Cleaning is not effective in inaccessible areas, such as the underside of trays, due to poor contact with the cleaning solution. Contact may be improved by injecting air or nitrogen at the base of the column. If steam is used to heat the chemicals, the location of the steam injection point should not lead to localized overheating. High temperature can also increase corrosion in the vapor space.

7.19.1.4 Foam Cleaning

This uses a static foam generator that employs air or nitrogen to produce a foamed solvent. Foam stabilizers are required to prolong foam life and increase the effectiveness of the cleaning chemicals. Foam cleaning is used on equipment that cannot support full or partial filling with liquid. Foam cleaning results in significantly less liquid volume for disposal, compared with other methods.

7.19.1.5 Vapor-Phase Organic Cleaning

Vapor-phase organic cleaning is used in equipment that is difficult to clean with liquids. For example, vaporized organic solvents are used to remove organic deposits from columns. The organic solvent is vaporized, injected into the top of the column, condensed, collected in a circulation tank, and revaporized. The principal concerns are the handling and disposal of the solvent and its flammability (when applicable). The recirculating tank should be purged and blanketed with nitrogen, fitted with an adequate venting and condensing system, and grounded to prevent accumulation of an electrical charge.

7.19.1.6 Steam-Injected Cleaning

Steam-injected cleaning involves the injection of a concentrated mixture of cleaning chemicals into a stream of fast-moving steam. The steam is injected at one end of the system and condensed at the other. It atomizes the chemicals, increasing their effectiveness, and ensures good contact with the metal surface.

Steam-injected cleaning is very effective for critical piping systems. As with foam cleaning, the method produces a relatively low amount of liquid for disposal.

7.19.2 Chemical Cleaning Solutions

A wide variety of standard chemical cleaning solutions are available (Table 7.8). Many proprietary solutions are based on these chemicals. Some are patented or involve patented equipment. Chemical cleaning contractors are the best source of information on standard or patented techniques, (see also industrial cleaning manual, TPC-8 NACE).

Most chemical cleaning contractors calculate the concentration of chemicals in weight percent, but some use volume percent. The user must be aware of this. For example, a 10 wt% solution of HCl is equivalent to 25 vol% of the normal 30% concentrated HCl.

Chemical cleaning solutions include mineral acids, organic acids, bases, complexing agents, oxidizing agents, reducing agents, and organic solvents. Inhibitors and surfactants are added to reduce corrosion and to improve cleaning efficiency. Following the cleaning cycle, a passivating agent can be introduced to prevent further corrosion or to remove trace ion contamination.

Mineral acids are strong scale dissolvers. They include HCl, hydrochloric/ammonium bifluoride (HCl/NH_4HF_2), sulfamic acid (NH_2SO_3H), HNO_3, phosphoric acid (H_3PO_4), and H_2SO_4.

Organic acids are much weaker. They are often used in combination with other chemicals to complex scales. An advantage of organic acids is that they can be disposed of by incineration. They include formic (HCOOH), hydroxyaceticformic, acetic (CH_3COOH), and citric acid.

Bases are principally used to remove grease or organic deposits. They include alkaline boil-out solutions and emulsions. Complexing agents are chemicals that combine with metallic ions to form complex ions, which are ions having two or more radicals capable of independent existence. Ferricyanide $[Fe(CN_6)]^{3-}$ is an example of a complex ion. Complexing agents are of two types: chelants and sequestrants. Chelants complex the metallic ion into a ring structure that is difficult to ionize, and sequestrants complex the metallic ion into a structure that is water soluble.

Table 7.8 *Scales and solvents*

Scale component	Solvent*	Testing conditions
Iron oxide	5 to 15% HCl	65–80 °C (150–175 °F)
Fe_3O_4 (Magnetite or mill scale)	2% hydroxyacetic/formic	65–80 °C (150–175 °F) Circulating
Fe_2O_3 (red iron oxide or red rust)	Monoammoniated citric acid	85–105 °C (185–220 °F) Circulating
	Ammonium EDTA	75–150 °C (170–300 °F) Circulating
	EDTA organic acid mixtures	40–65 °C (100–150 °F) Circulating
Copper, oxides	Copper complexer in HCl	65 °C (150 °F)
	Ammoniacal bromate	50–85 °C (120–185 °F)
	Monoammoniated citric acid	60–85 °C (140–185 °F) pH 9 to 11
	Ammonium persulfate	Below 40 °C (100 °F)
	Ammonium EDTA	65–80 °C (150–185 °F) pH 9 to 11
Calcium carbonate	5 to 15% HCl	Preferably not above 65 °C (150 °F)
	7 to 10% sulfamic acid	Do not exceed 60 °C (140 °F)
	Sodium EDTA	60–150 °C (150–300 °F) Circulating
Calcium sulfate	Sodium EDTA	60–150 °C (150–300 °F) Circulating
	1% NaOH–5% HCl	50–65 °C (120–150 °F) Circulating
	EDTA organic acid mixtures	40–65 °C (100–150 °F) Circulating
Hydroxyapatite of phosphate compounds ($Ca_{10}(OH)_2.(PO_4)_6$)	5 to 10% HC	Preferably above 65 °C (150 °F)
	Sodium EDTA	Undesirable to add fluoric 65–150 °C (150–300 °F) Circulating
	Sulfamic acid 7 to 10%	Do not exceed 60 °C (140 °F)
Silicate compounds, e.g., acmite ($NaFe(SiO_3)_2$) and analcite ($NaAlSi_2O_6.H_2O$)	Prolonged treatment with 0.5 to 1% soda ash at 345 kPa (50 psi), followed by HCl containing fluoride	Alkaline preboil at 345–690 kPa (50–100 psi) for 12 to 16 h
Pedtolite ($4Ca.Na_2O.6SiO_2.H_2O$)	HCl containing ammonium bifluoride	65–80 °C (150–175 °F)
Serpentine ($Mg_3Si_2O_7.2H_2O$)	HCl, inhibited	Heat slowly to avoid sudden release of H_2S toxic gas
Sulfides ferrous: troilite (FeS) and pyrrhotite (FeS)		
Disulfides: FeS_2, marcasite and pyrite	Chromic acid, followed by HCl	Boiling 7 to 10% chromic acid, followed by inhibited HCl
Organic residues Organo lignins Algae Some polymeric residues	Potassium permanganate followed by HCl containing oxalic acid or chlorine gas	Circulate at 100 °C (210 °F), add 1 to 2% $KMnO_4$ solution. Oxalic acid added to HCl controls release

*The chemicals listed should be considered possible solvents only. There are many alternative solvents for each deposit listed.

Oxidizing agents are used to oxidize compounds present in deposits to make them suitable for dissolution. They include chromic acid (H_2CrO_4), potassium permanganate ($KMnO_4$), and sodium nitrite ($NaNO_2$).

Reducing agents are used to reduce compounds in deposits to a foam that makes them suitable for dissolution and to prevent the formation of hazardous by-products. They include sodium hydrosulfite ($NaHSO_2$) and oxalic acid.

Inhibitors are specific compounds that are added to cleaning chemicals to diminish their corrosive effect on metals. Most inhibitors are proprietary, and recommendations for their use are available from the supplier.

Surfactants are added to chemical cleaning solutions to improve their wetting characteristics. They are also used to improve the performance of inhibitors, emulsify oils, improve the characteristics of foaming solvents, and act as detergents in acid and alkali solutions. As with inhibitors, most surfactants are proprietary products.

8

Corrosion Inhibitor Evaluations

Oil and gas production operations utilize a tremendous amount of iron and steel materials. These materials are in the form of pipes, tubing, casing, pumps, valves, and other accessories that are susceptible to corrosion, depending on the composition and characteristics of the produced fluids.

One of the major ways of protecting oil and gas production and operating systems against corrosion is by applying corrosion inhibitors. The corrosion inhibitors are evaluated in order to determine if the corrosion preventive measures applied are necessary, and if the required lifetime can be achieved with a particular inhibitor, as the effective life of corrosion inhibitors varies with the quantity of water intrusion. The purpose of this chapter is to evaluate the on-line monitoring of corrosion and corrosion inhibitor effectiveness under different conditions.

8.1 On-Line Monitoring of Corrosion

The concept of corrosion monitoring has developed from two distinct areas, plant inspection techniques, and laboratory corrosion testing techniques, with the original aim of assessing or predicting corrosion.

Corrosion monitoring data are used for following purposes:

- To monitor the effectiveness of a solution. A logical extension of the diagnostic application is to use corrosion monitoring techniques to establish whether a solution has been effective. This can be done simply by continuing the original investigation, but more permanent installations are being used to an increasing extent to provide long-term assurance. Such equipment is likely to be more sophisticated, since the information is recorded with other operational data and interpreted, in the first instance at least, by staff with a more limited corrosion knowledge.
- To provide operational or management information. Corrosion can often be controlled by maintaining a single operational variable (e.g. temperature, pH, humidity) within limits determined by prior monitoring or other investigations. If the significant variable is measured for other reasons, this measurement can be used directly for corrosion control. If the variable is not otherwise measured,

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or in more complex cases where several variables interact, corrosion monitoring information can be used by plant operators to control plant operation so as to control corrosion. Any process change may have significant effects on corrosion, and corrosion monitoring techniques allow full-scale trials to proceed with minimum risk to the plant.

8.2 Corrosion Monitoring Techniques

A wide range of corrosion monitoring techniques is now available, allowing determination of total corrosion, corrosion rate, corrosion state, analytical determination of corrosion product or active pieces, detection of defects, or changes in physical parameters. Associated costs can be small where simple instrumentation and a few measurements are appropriate, but in some cases may be extremely costly and require expert skills.

Much of the progress made in the past few years has been due to advances in electronics that have allowed multi-probe measurement and recording at a tolerable cost. Instantaneous feedback of corrosion information can be obtained, from various parts of the plant, that can be fed to the plant control room and/or plant computer to permit control of the necessary process variable to provide corrosion control. Table 8.1 indicates corrosion monitoring techniques available, some of which are described in more detail.

8.3 Selecting a Technique for Corrosion Monitoring

Many techniques have been used for corrosion monitoring (see Table 8.1), it is clearly possible to develop others. Consequently, when a possible new application is being considered, a problem arises in choosing the most appropriate technique. Each has its strong points and its limitations, and none is the best for all situations.

Any monitoring technique can provide only a limited amount of information, and the techniques should be regarded as complementary rather than competitive. Where more than one technique will give the information required, the information is obtained in different ways; a cross-check can be valuable and differences in detail can add meaning.

A corrosion monitoring technique rarely gives wrong information, unless the equipment used is faulty. “Nonsense” results arise because the information is correct, but irrelevant in the corrosion sense. The polarization resistance method, for example, measures the combined rate of any electrochemical reactions at the surface of the test sample. If the main reactions are corrosion, the rate measured is the corrosion rate. If however, other reactions are possible at rates that are comparable or greater, the measured rate includes the other reactions.

Useful deductions can still be made provided it is recognized that the corrosion rate has not been measured. The choice of a monitoring technique is a complex problem requiring expert knowledge. The first essential is to establish what type of information is needed. This necessarily involves an input from the management of the plant in question. The information below will give general guidance.

8.3.1 Where the Primary Objective is Diagnosis in a New Situation

Typically the nature of the corrosion processes involved and the controlling parameters are uncertain. It may be difficult to decide on the most appropriate technique, but it is in any case often advantageous

Table 8.1 *Methods and techniques for corrosion monitoring*

Method	Measures or detects	Notes	Use
Linear polarization (polarization resistance)	Corrosion rate is measured by the electrochemical polarization resistance method with two or three electrode probes	Suitable for most engineering alloys providing the process fluid is of suitable conductivity. Portable instruments at modest cost, to more expensive automatic units are available	Frequent
Electrical resistance	Integrated metal loss is measured by the resistance change of a corroding metal element. Corrosion rates can be calculated	Suitable for measurements in liquid or vapor phase on most engineering metals and alloys. Probes as well as portable and more expensive multi-channel units are available	Frequent
Potential monitoring	Potential change of monitored metal or alloy (preferably plant) with respect to a reference electrode	Measures directly state of corrosion of plant, e.g. active, passive, pitting, stress corrosion cracking, via use of a voltmeter and reference electrode	Moderate
Corrosion coupon testing	Average corrosion rate over a known exposure period by weight loss or weight gain	Most suitable when corrosion is at a steady rate. Indicates corrosion type. Moderately cheap method with corrosion coupons and spools readily made	Frequent
Analytical	Concentration of the corroded metal ions or concentration of inhibitor	Can identify specific corroding equipment. Wide range of analytical tools available. Specific ion electrodes readily used.	Moderate
Analytical	pH of process stream	Commonly used in effluents. Standard equipment available through robust pH responsive electrodes such as antimony, platinum, tungsten can be preferable to glass electrodes. Solid Ag/AgCl is a useful reference electrode	Frequent
Analytical	Oxygen concentration in process stream	Useful where oxygen control against corrosion using oxygen scavengers, such as bisulfite or dithionite, is necessary. Electrochemical measurement	Moderate
Radiography	Flaws and cracks by penetration of radiation and detection on film	Very useful for detecting flaws in welds. Requires specialized knowledge and careful handling	Frequent

(*continued overleaf*)

Table 8.1 *(continued)*

Method	Measures or detects	Notes	Use
Ultrasonics	Thickness of metal and presence of cracks, pits, etc. by changes in response to ultrasonic waves.	Widely used for metal thickness and crack detection. Instrumentation is moderately expensive, but simple jobs contracted out at fairly low cost	Frequent
Eddy current testing	Uses a magnetic probe to scan surface	Detects surface defects such as pits and cracks with basic instrumentation of only moderate cost	Frequent
Infrared imaging (thermography)	Spot surface temperatures or surface temperature pattern as indicator of physical state of object	Used most effectively on refractory and insulation furnace tube inspection. Requires specialized skills and instrumentation is costly	Infrequent
Acoustic emission	Leaks, collapse of cavitation, bubbles, vibration level in equipment. Cracks by detection of the sound emitted during their propagation	A new technique capable of detecting leaks, cavitation, corrosion fatigue pitting and stress corrosion cracking in vessels and lines	Infrequent
Zero resistance ammeter	Galvanic current between dissimilar metal electrodes in suitable electrolyte	Indicate polarity and direction of bimetallic corrosion. Useful as dewpoint detector of atmospheric corrosion or leak detection behind linings	Infrequent
Hydrogen sensing	Hydrogen probe used to measure hydrogen gas liberated by corrosion	Used in mild steel corrosion involving sulfide, cyanide and other poisons likely to cause hydrogen embrittlement	Frequent in petrochemical industry
Sentinel holes	Indicates when corrosion allowance has been consumed	Useful in preventing catastrophic failure due to erosion at pipe bends, etc. Leaking hole indicates corrosion allowance has been consumed	Infrequent

to use more than one. The factors that actually prove to be significant are not always those that would have been expected.

One approach is to undertake a laboratory study to determine which parameters are likely to be important, the information being used, both to decide which techniques should be used on the plant and to aid interpretation of the results obtained on the plant.

Alternatively, monitoring can be undertaken directly. The choice between these approaches depends on the availability of suitable laboratory facilities and staff with the necessary experience,

and on the extent to which the problem is understood. In either case, it is sensible to check the information obtained by monitoring; by inspection before and after, or other means.

Expert help is often necessary in interpretation of the results and may be desirable in planning the work and selection of techniques. However successful interpretation requires knowledge of the plant and process in question, as well as expertise in monitoring techniques and knowledge of corrosion.

8.3.2 Where the Primary Objective is to Monitor the Behavior of a Known System

Applications of this type often follow one of the diagnostic types; alternatively the problem resembles other cases where monitoring has been used successfully. In either case, the choice of technique is based on past experience. Expert assistance may well be unnecessary, even in interpretation of the results, unless unusual features appear.

In addition to choosing the technique, it is necessary to decide the degree of complexity that is appropriate. The basic monitoring equipment for most techniques is relatively simple, comprising a probe (the sensing element) and a measuring instrument. The equipment cost is relatively modest, as is the labor cost, if only a few readings are required. The amount of information that can be obtained by this approach is limited, but may be sufficient. If not, additional probes can be installed and/or more complex instrumentation introduced to enable automatic scanning, automatic recording, or regular readings from one or more probes and control panel displays.

8.3.3 Criteria for Selection of Technique

Eight criteria on which the choice of a technique depends are summarized in Table 8.2 for the various corrosion monitoring methods and described below.

8.3.3.1 Time for Individual Measurement

Some techniques provide information that is effectively instantaneous, while others are necessarily slower in this respect.

8.3.3.2 Type of Information Obtained

Some techniques provide a measurement of corrosion rate, others measure total corrosion, or the remaining thickness, which is not exactly equivalent; yet others provide information on the distribution of corrosion on the corrosion regime.

8.3.3.3 Speed of Response to Change

Techniques that do not provide an individual measurement quickly are obviously unsuitable for situations where a fast response is required. Not all techniques that provide effectively instantaneous information are capable of a fast response, however. Where the measurement is of rate of corrosion, a fast response can be obtained, but if the measurement is of total corrosion, remaining thickness, or distribution of corrosion, the speed of response is limited by the ability of the technique to discriminate between successive readings.

8.3.3.4 Relation to Plant Behavior

Many of the more effective techniques provide information on the behavior of a probe inserted into the plant, which does not necessarily reflect the behavior of the plant itself. The information obtained is in fact a measure of the corrosivity of the environment, from which plant behavior can be inferred.

Table 8.2 *Characteristics of corrosion monitoring techniques*

Technique	Time for individual measurement	Type of information	Speed of response to change	Relation to plant
Electrical resistance	Instantaneous	Integrated corrosion	Moderate	Probe
Polarization resistance	Instantaneous	Rate	Fast	Probe
Potential measurement	Instantaneous	Corrosion state and indirect indication of rate	Fast	Probe or plant in general
Galvanic measurements (zero resistance ammeter)	Instantaneous	Corrosion state and indication of galvanic	Fast	Probe or occasionally plant in general
Analytical methods	Normally fairly fast	Corrosion state, total corrosion in system item corroding	Normally fairly fast	Plant in general
Acoustic emission	Instantaneous	Crack propagation and leak detection	Fast	Plant in general
Thermography	Relatively fast	Distribution of attack	Poor	Localized on plant
Optical aids (closed circuit TV, light tubes, etc.)	Fast when access available, otherwise slow	Distribution of attack	Poor	Localized on plant
Visual, with aid of gages	Slow; requires entry on shutdown	Distribution of attack indication of rate	Poor	Accessible surfaces
Corrosion coupons	Long duration of exposure	Average corrosion rate and form	Poor	Probe
Ultrasonics	Fairly fast	Remaining thickness or presence of cracks and pits	Fairly poor	Localized on plant
Hydrogen probe	Fast or instantaneous	Total corrosion	Fairly poor	Localized on plant or probe
Sentinel holes	Slow	Go/no-go remaining thickness	Poor	Localized on plant
Radiography	Relatively slow	Distribution of corrosion	Poor	Localized on plant
Technique	Possible environments	Type of corrosion	Ease of interpretation	Technological culture needed
Electrical resistance	Any	General	Normally easy	Relatively simple
Polarization resistance	Electrolyte	General	Normally easy	Relatively simple

Potential measurement	Electrolyte	General or localized	Normally relatively easy, but needs knowledge of corrosion; may need expert	Relatively simple
Galvanic measurements (zero resistance ammeter)	Electrolyte	General or unfavorable conditions localized	Normally relatively easy, but needs knowledge of corrosion	Relatively simple
Analytical methods	Any	General	Relatively easy, but needs knowledge of plant	Moderate to demanding
Acoustic emission	Any cavitation	Cracking, cavitation and leak detection, pitting	Normally easy	Crack propagation specialized, otherwise relatively simple
Thermography	Any; must be warm or sub-ambient	Localized	Easy	Specialized and difficult
Optical aids (closed circuit TV, light tubes, etc.)	Any	Localized	Easy	Relatively simple
Visual, with aid of gages	Any	General or localized	Easy	Relatively simple, but experience needed
Corrosion coupons	Any	General or localized	Easy	Simple
Ultrasonics	Any	General or localized	Easy	Simple
Hydrogen probe	Non-oxidizing electrolyte or hot gases	General	Easy	Simple
Sentinel holes	Any, gas or vapor preferred	General	Easy	Relatively simple
Radiography	Any	Pitting possibly, cracking	Easy	Simple, but specialized radiation hazard

Other techniques provide an indication of the total corrosion in the system, with little or no indication of its distribution, and some give an accurate picture of a local corrosion pattern of the plant itself, but no information on what is happening elsewhere.

8.3.3.5 Applicability to Environments

A fast response is most readily obtained from electrochemical measurements that require that the environment is an electrolyte; a high electrolytic conductivity is not always necessary, however. Non-electrochemical measurements can be used in gaseous environments, or non-conducting fluids, as well as in electrolytes.

8.3.3.6 Type of Corrosion

Most corrosion monitoring techniques are best suited to situations where corrosion is general, but some provide at least some information on localized corrosion.

8.3.3.7 Difficulty of Interpretation

Interpretation of the results is often relatively straightforward if the technique is used within its limitations. The interpretation of the results obtained by some techniques is, however, more difficult, and this is true of all techniques if they are used near the limits of their applicability.

8.3.3.8 Technological Culture

Some techniques are inherently technically sophisticated; this tends to limit their use to organizations with a strong technological culture. Most others are much less demanding in this respect.

In principle, the available techniques could be ranked in order or merit for each of these eight criteria. In practice, the relative merits change with circumstances so that a formal treatment of this type is potentially misleading. The most useful general approach is therefore, to consider the strengths and weaknesses of the techniques individually and Table 8.2 provides a reasonable starting point.

8.4 Corrosion Monitoring Strategy

One of the critical components of corrosion monitoring is analyzing the samples taken from the process stream and reporting accurate and relevant data to the system operators.

A comprehensive review of the process plant materials, corrosion allowances, and operating conditions should be carried out to identify all areas that could be susceptible to significant corrosion within the projected lifespan of the plant. An assessment of the consequences of a corrosion failure occurring will be an integral part of the review.

The identification of the specific corrosion processes likely to occur is essential to the selection of particular on-line corrosion monitoring devices to be used. The review should also identify those parameters that are instrumental in causing corrosion and that are likely to influence the corrosion rate. The results of the review should be used to develop a corrosion monitoring strategy encompassing the following:

- Identification and location of monitoring devices and their location
- Prescribed monitoring frequencies
- Agreed monitoring procedures
- The allocation of responsibilities for:

- ensuring that monitoring is carried out in accordance with the defined procedures,
- the interrogation, storage and retrieval of the information recorded,
- the presentation of detailed reports at the required frequency.

For new projects, the corrosion monitoring requirements should be established during the early development of the design.

8.4.1 Equipment

The selection of the specific on-line corrosion monitoring devices will be determined by the known or perceived corrosion processes taking place.

Individual corrosion monitoring devices provide only a limited amount of information. A minimum of two techniques should be used to monitor corrosion in order to provide complementary data. In addition, the information provided by the corrosion monitoring devices should be supplemented by detailed operational data covering the monitoring period, chemical analysis of process fluids, and equipment inspection records.

On-line internal corrosion monitoring should be undertaken using proprietary access fittings that permit the installation and removal of probes and coupons without the need for plant shut-down. The design and mechanical properties of such fittings must meet the requirements of the appropriate standard(s) and code(s) used for the design and construction of the plant being monitored.

8.4.2 Weight Loss Coupons

Coupons may be used to determine the average fluid corrosivity by measurement of weight loss (See Figure 8.1). Susceptibility to pitting, bimetallic corrosion, stress corrosion cracking, crevice corrosion, corrosion in weldments or heat affected zones (HAZ), hydrogen embrittlement, scaling, erosion, and cavitation may also be determined. The method facilitates an assessment of the corrosivity of an environment with respect to the specific material of construction of that part of the plant.

A data report is generated upon completion of the coupon analysis and is available to the client by electronic mail, diskette, mail, courier, or facsimile. Results are not limited to corrosion rates,

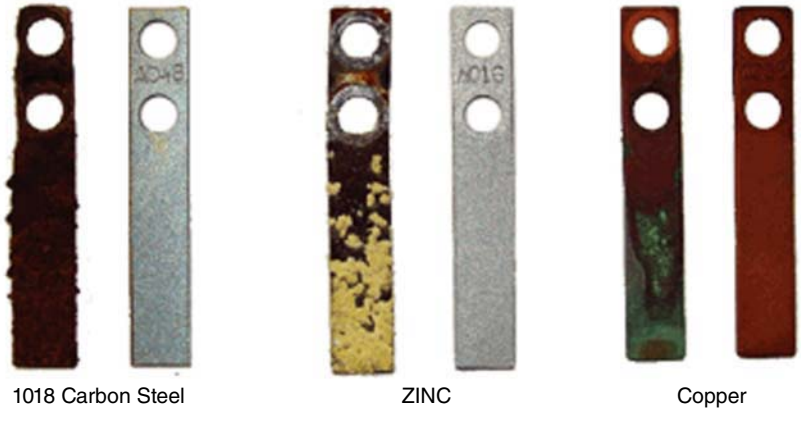


Figure 8.1 *Samples of carbon steel, zinc, and copper coupons. (Reproduced with permission from Analog © Luis Orozco.)*

but may also include information specific to the corrosion mechanism encountered, such as pitting, scale build-up, and severity of attack. All analysis is completed in accordance with industry and/or customer standards.

The chemical composition and metallurgical condition of the coupon material should be as close as possible to that of the plant material. The results may be influenced significantly by the monitoring location within the plant and the position of the coupon(s) in the process stream, see NACE RP0775.

Careful consideration should be given to the proposed monitoring location and coupon position during the development of the corrosion monitoring strategy. The two most common types of weight loss coupon are strip and flush disc, although rods and rings may also be used in certain circumstances. Guidance on coupon selection, handling exposure times, and evaluation are given in NACE RP0775.

Each coupon should carry its own individual identification mark and be degreased and uniformly grit blasted prior to exposure. Where considered appropriate "as finished" metal surfaces may be evaluated, but these are likely to give inconsistent results.

For purposes other than weight loss from a single metal or alloy, (e.g. bimetallic corrosion, weldment corrosion, stress corrosion cracking), novel coupon designs will be required, appropriate to the corrosion phenomenon being evaluated.

Coupons should be attached to holders suitable for installation in low-pressure or high-pressure (50 mm) access fitting systems as appropriate. Exposed coupons should always be visually examined for the type and uniformity of the attack, both before and after chemical cleaning. Samples of corrosion product should be removed for detailed chemical analysis. Where pitting is the predominant form of attack, the extent and type of pitting may be evaluated in accordance with ASTM G46-76.

8.4.3 Spool Pieces

To obtain a direct assessment of the corrosivity of a process stream, the piping system may be configured to include short lengths of flanged pipework (0.3 to 1.0 m), which can be removed periodically for internal inspection. These spool pieces should be fabricated from an identical piping material to the adjacent pipework. Where spool pieces with different piping materials are to be evaluated, the extent of any galvanic couple between adjacent piping and spools must be assessed and electrical insulation requirements established as appropriate.

The piping spools should be cleaned prior to exposure and may also be weighed, where the measurement of weight loss is considered practical. If weight loss is to be determined, then the spools must be protected from external corrosion or mechanical damage while in service.

After exposure, the spool piece should be cleaned internally using the methods described for corrosion coupons in NACE RP0775 and, where appropriate, re-weighed in order to calculate the overall corrosion rate. Sectioning will be required to enable a detailed visual assessment of the metal loss to be made. Localized corrosion should be evaluated in accordance with ASTM G46-76.

8.4.4 Field Signature Method (Electric Fingerprint)

This comprises the measurement of the changes in an applied electric field within a pipe spool, caused by the loss of material from the inner wall due to internal corrosion. Field signature methods are commercially available.

Thin contact pins, typically up to 64 in number, are welded or cemented to the outside of the pipe wall in a configuration that is determined by the position and the pattern of internal corrosion expected.



Figure 8.2 *Sample electrical resistance (ER) corrosion probes. (Reproduced with permission from Daubert Cromwell.)*

Each pin is connected to a data acquisition unit that monitors the potential difference generated between individual pairs of pins as a consequence of the application of an external current between two auxiliary pins spanning the measurement pin configuration.

Using appropriate software the change in the "fingerprint coefficient" with time for each pair of pins enables a graphical representation of the corrosion pattern to be developed with quantitative estimates of the loss in wall thickness across the area covered by the pin array.

The technique has the advantage that it measures the actual corrosion taking place within the process system, regardless of process fluid type and with a high degree of sensitivity, without the need for access fittings, intrusive probes, and retrieval operations. Removal of the spool piece for confirmation of the pattern and extent of corrosion being indicated is recommended. This will normally have to coincide with a plant shut-down.

Careful thought must be given to the overall pattern and the individual spacing of the pins in order to generate the optimum information from the data recorded.

The magnitude of the current applied between the auxiliary pins is dependent upon wall thickness and needs to be adjusted accordingly, to maximize the accuracy of the data.

8.4.5 Electrical Resistance Probes

Electrical resistance (ER) corrosion probes are commonly used in petroleum, chemical processing, and other environments where on-line corrosion rate readings are required (see Figure 8.2). Whereas test coupons must be removed from the process for evaluation, corrosion probes can allow corrosion rate determination without probe removal. Probes can be manufactured according to specific requirements for temperature, pressure, and other conditions. Hydrogen, sampling, injection, and custom-designed probes can be made as well.

Electrical resistance probes measure the change in electrical resistance of a sacrificial element exposed to the process fluid relative to a reference element sealed within the probe body. If the probe corrodes uniformly, the change in resistance of the exposed element over a fixed time period is directly proportional to the average corrosion rate for that period.

Successive readings must be compared in order to determine fluid corrosivity over the intervening period. Electrical resistance probes may be used to measure the corrosivity of both conductive and non-conductive liquids and vapors. There are three main types:

- Tubular element
- Wire loop
- Flush.

Of the three types the tubular element is the most commonly used. Wire loop probes are less robust than their tubular element counterparts and are more susceptible to mechanical damage. Flush mounted probes can suffer preferential crevice attack at the steel element/potting compound interface, which can give rise to unrepresentative corrosivity data.

Under high-velocity process conditions, tubular element and wire loop probes may require velocity shields for protection. However, velocity shields are prone to debris accumulation with attendant spurious results from the probe and their use should be limited accordingly.

Wire loop or tubular element electrical resistance probes, fitted with velocity shields that extend the full length of the probe body, should not be used in conjunction with low-pressure access fittings on hydrocarbon or other hazardous duty. There is a risk that an uncontrolled fluid release could occur on retracting the probe, should the velocity shield fail by a corrosion-related or other mechanism.

8.4.6 Electrochemical Probes

The linear polarization resistance (LPR) technique is based upon the measurement of the "apparent resistance" of a corroding electrode when it is polarized by a small voltage of the order of 10 millivolts. The apparent resistance is determined from the current flowing as a consequence of the small applied voltage and is inversely proportional to the corrosion rate.

LPR probes have the advantage over electrical resistance probes in that they provide an instantaneous measurement of fluid corrosivity. However, they can only be used to measure the corrosivity of "clean," low-resistivity process fluids under conditions of continuous immersion.

The limits of operation of the technique are also governed by the expected corrosion rate, and advice should be sought from the probe supplier. As the electrochemical characteristics of LPR probe elements may change with corrosion of the elements, probes should be replaced on a more frequent basis (than for electrical resistance probes) in order to ensure that consistent data is being produced. LPR probes may also suffer from "shorting out" due to the accumulation of debris or corrosion products bridging the gap between the electrodes.

LPR probes are available in the form of two or three rod-like electrode assemblies, with the rods protruding into the process stream. Three-electrode assemblies are used where a high corrosion rate is anticipated in a low-conductivity fluid, and where there would be a significant contribution to the measured polarization resistance from the electrolyte resistance.

Three-electrode probes are normally used where the fluid conductivity is less than 100 micro ohms (fluid resistivity greater than 104 ohm cm). Flush mounted versions are also available in various two electrode configurations. As with electrical resistance probes the flush mounted versions can be susceptible to crevice corrosion at the electrode/potting compound interface and may give unrepresentative corrosivity values.

8.4.7 Electrochemical Noise

This technique of corrosion monitoring utilizes three electrode linear polarization probes, but is more sensitive than LPR measurement. It records the random fluctuations in current and/or potential

(electrochemical noise) generated by corrosion reactions taking place at the surfaces of the probe elements. Unlike the LPR method, the electrodes are not polarized, but allowed to corrode freely in the process stream.

The technique is very sensitive to changes in processing conditions that affect the corrosivity of the fluids and is particularly useful for optimizing corrosion inhibitor/chemical treatment programs. However, as the same probe configuration is used for the measurement of electrochemical noise as for the LPR method, the technique suffers from the same disadvantages.

8.4.8 Solid Particle Impingement Probes

Sensors for the evaluation of solids entrained in fluid systems are available in two versions, intrusive and non-intrusive.

Intrusive solid particle impingement probes are available that can be located within standard 5.08 cm high-pressure access fittings. These probes work on a similar principle to electrical resistance probes, in that the change in electrical resistance with time due to the abrasive wear of the probe element is taken as proportional to the solids concentration of the fluid.

Derived formulas that include the average particle size, the flow velocity, and, where applicable, gas–liquid ratio enable a measure of the solid particle concentration to be made. In general, this type of probe suffers from a problematic sensitivity–lifespan relationship. Probes sensitive enough to give useful data require frequent change out due to their finite lives.

Non-intrusive solid particle impingement probes comprise a sensor that is strapped to the outside of the pipe wall in an area where particle impingement is judged to be greatest. Two types of sensor can be used to detect particle impacts, ultrasonic and stress wave.

Ultrasonic sensors record the magnitude of the noise generated by the particle impacts and appropriate computer software is used to convert the ultrasonic signals to give a measure of solid particle content. In the alternative technique, stress wave sensors in acoustic contact with the pipe wall count the number of acoustic pulses generated by the particle impacts on the inner wall of the pipe. The acoustic pulses or stress waves generated have a typical frequency of 500 kHz. Stress wave sensors have the advantage that the pulse counting method suppresses the influence of erroneous signals produced by, for example, pipe vibration, which can be a significant problem with ultrasonic sensors.

8.4.9 Hydrogen Probes and Patch Monitors

Hydrogen is the product of corrosion reactions in many systems, but most significantly where the process streams contain water and H_2S, HCN, or HF.

The combination of hydrogen atoms to form hydrogen gas at the corroding metal surface is retarded by certain anions, the most common being sulfide, cyanide, and fluoride. These anions thereby promote the diffusion of atomic hydrogen into the steel substrate.

Equipment for measuring the rate of diffusion of atomic hydrogen into structural materials is available in two forms, either as thin-walled tubular probes inserted directly into the process stream through standard 5.08 cm (2 inch) high pressure access fittings, or as patch detectors clamped or welded to the outer pipe or vessel wall.

Intrusive thin-walled hydrogen probes collect the hydrogen diffusing through the wall of the probe element. An integral pressure gage is used to monitor the pressure build-up arising from arrival of atomic hydrogen at the inner wall of the probe element, where the atoms combine to form hydrogen gas.

The rate of pressure build-up can be related to the potential for hydrogen damage occurring in the vessel or piping materials. A period of stabilization is required to enable the tubular element to saturate with atomic hydrogen before meaningful data can be accumulated.

There are two types of non-intrusive hydrogen patch probes. The first comprises a carbon steel patch contoured to fit the outside of the vessel or pipe, and welded to it.

The patch is fitted with temperature and pressure gages and the quantity of hydrogen diffusing directly through the vessel or pipe wall is measured by logging the rate of increase in pressure within the patch envelope in an analogous manner to the tubular element hydrogen probe. The second type of patch probe is mounted directly onto the vessel or pipe wall using mechanical straps.

The probe comprises a small electrochemical cell with one electrode, a thin inert metal foil, usually palladium, in direct contact with the pipe wall. As the hydrogen diffuses through the vessel or pipe wall and the metal foil, it is electrochemically oxidized on the inner face of the foil that is in contact with the cell electrolyte. The current flowing in the cell is directly proportional to the rate of hydrogen permeation through the wall of the equipment and provides a direct measure of hydrogen activity.

As with the other types of hydrogen probe described above, the electrochemical patch probe requires an initial stabilization period. In addition, it requires regular maintenance in the form of electrolyte replenishment and/or renewal.

8.4.10 Galvanic Probes

Probes comprising two dissimilar metals may be used to assess the corrosivity of a conductive process fluid (see Figure 8.3). The natural current flow between the two metals is measured using a zero resistance ammeter and the magnitude of the current gives a measure of fluid corrosivity.

Direct correlations between the corrosivity of the fluid measured by a galvanic probe and the performance of the less noble constituent of an equivalent bimetallic couple that exists within the process plant should be made with care, as the surface area ratio between the two metals is critical in determining the magnitude of the galvanic effect.

Conventional galvanic probes comprising a brass cathode and mild steel anode are sensitive to the concentration of oxidizing species in conductive fluids and may be used to monitor the level of dissolved oxygen and the effectiveness of oxygen scavengers in water injection and cooling water systems.

Galvanic probes comprising parent metal, weld metal, and heat affected zone combinations may be used to assess the potential for preferential weldment corrosion within the process streams.

Such probes may comprise either five or six elements with the galvanic current between the various combinations of electrodes being recorded using a zero resistance ammeter.

Care is required in the manufacture of the probe elements to ensure that the welding processes used are comparable with those used in plant fabrication. Such probes are able to indicate the effect of changes in composition of the process fluids on the relative susceptibility of parent metal, heat affected zone, and weldment to internal corrosion.

8.4.11 Electrical Potential Monitoring

The measurement of the electrical potential between the piece of process equipment (or a probe of the same material) and a fixed reference electrode will provide information on the corrosion risks. The technique requires that the process fluid be conductive and the electrochemistry of the system well understood. Potential monitoring does not give a measure of the corrosion rate, but will indicate the

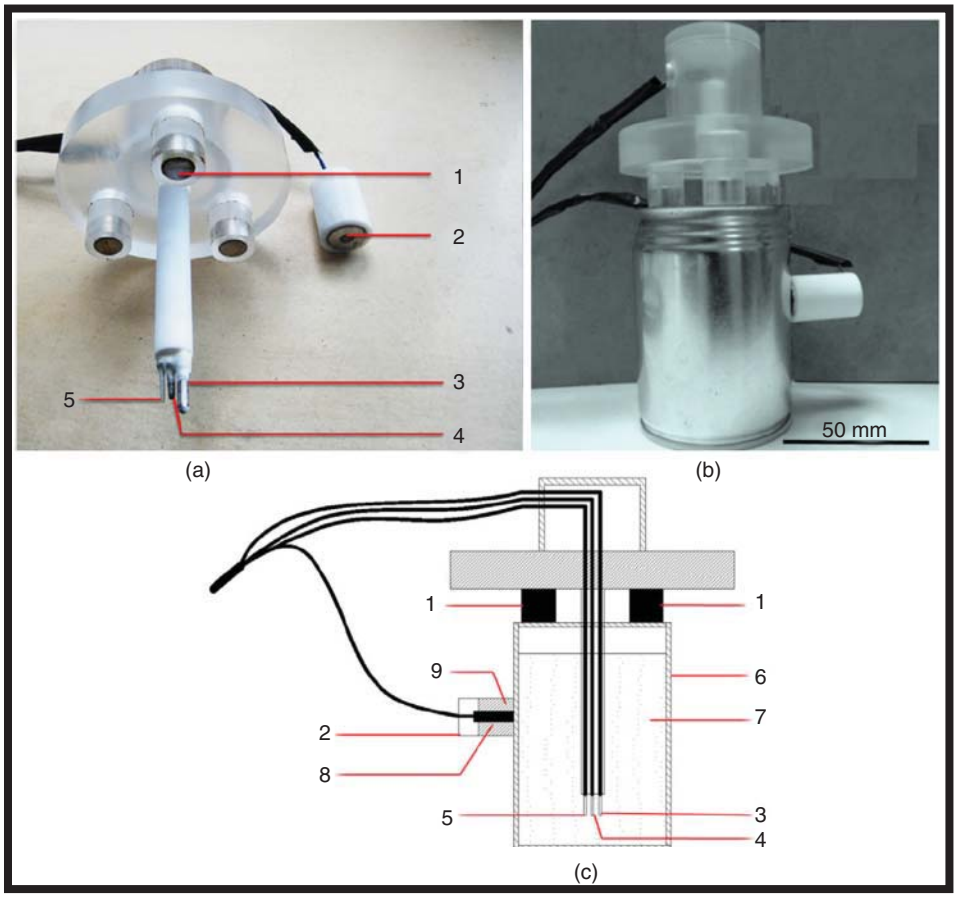


Figure 8.3 *The electrochemical sensor (a), corrosion detection of a beverage can (b), and a schematic diagram of the electrochemical cell (c). 1 – magnet; 2 – contactor of working electrode; 3 – counter electrode (platinized niobium) for EIS measurement; 4 – reference electrode; 5 – counter electrode (silicone rubber-coated platinum wire) for EN measurement; 6 – beverage can; 7 – beverage; 8 – copper bar; 9 – magnet. (Reprinted from D. Xia et al., 2012, with permission from Elsevier.)*

onset of active corrosion from an otherwise passive state due to changes in the processing conditions, where a clearly defined active–passive transition exists.

For practical purposes, a robust and stable reference electrode must be selected. The location of the test probe and the reference electrode may be critical to the provision of reliable information and require careful consideration. High-impedance voltmeters (> 1 megohm) should be used to record potentials, in combination with a chart recorder.

8.4.12 pH Probes

In aqueous process streams where the control of pH is critical either to the efficiency of the process or the resistance of the plant materials to corrosion, pH measurements may be used in conjunction with chemical treatment programs. Figure 8.4 shows A sample galvanic probe.



Figure 8.4 *A sample galvanic probe. (Reproduced with permission from Daubert Cromwell.)*

The removal of process fluid samples to a laboratory for pH measurement is not a reliable method of determining the system pH, since the pH of the sample may alter considerably as a consequence of the sampling procedures. For many applications on-line monitoring using pH probes is the only reliable method of monitoring unit or system pH.

The distance between the off-take point and the probe location should be kept as short as possible to minimize pressure drops that will affect the reliability of the pH measurement. The flow control and flow monitor should be placed downstream of the probe location to avoid sudden pressure drops that will encourage the release of gas from solution, the formation of gas pockets and gas blocking of the probe element. For similar reasons, long and tortuous sidestreams should be avoided. High flow rates through the sidestream will be beneficial in preventing the fouling of the probe element.

pH probes are prone to fouling, require frequent cleaning and calibration, and are more suited to installation in side streams or off-take lines rather than in a main process line or vessel. Figure 8.5 shows the location of a pH probe in a typical experimental facility.

8.4.13 Measurement of Dissolved Gases

Electrochemical probes are available that measure the concentration of dissolved oxygen in both conducting and non-conducting media. Care has to be taken in the selection of probe type, as with some the elements are easily poisoned by certain species within the process fluid.

The more reliable probes comprise a thin membrane that is porous to oxygen. The oxygen diffuses through the membrane and dissolves in the small body of electrolyte within the probe. The oxygen within the electrolyte is electrochemically reduced at an inert electrode and the corresponding current that flows between this and an auxiliary electrode gives a measure of the concentration of dissolved oxygen in the process fluid.

Dissolved oxygen probes should not normally be inserted directly into the process stream, but fitted into a small flow chamber connected to a side stream or a process fluid off-take point. Proprietary kits may be used for the rapid on-site determination of oxygen, carbon dioxide, and hydrogen sulfide levels in aqueous process fluids.

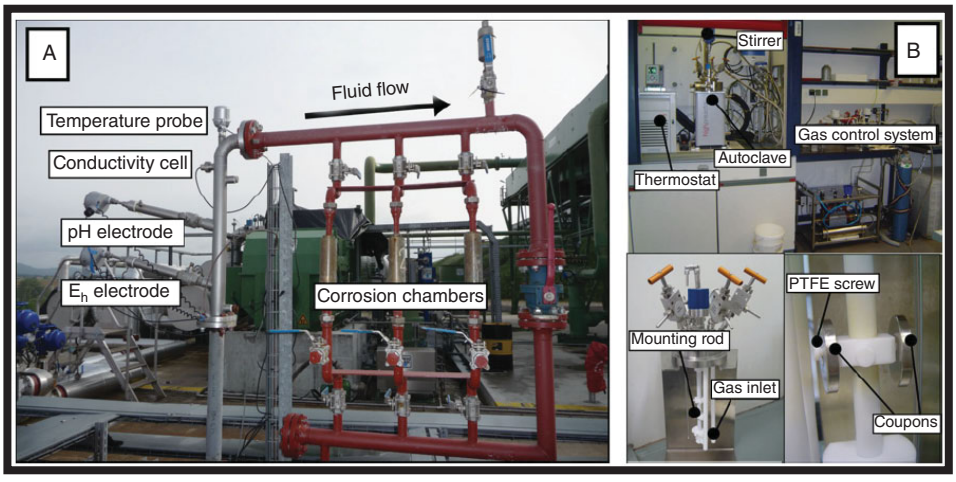


Figure 8.5 *Instrumentation for monitoring and corrosion experiments. (A) "geochemistry–corrosion" skid near the well head of GPK3 on the reinjection side of the Soultz geothermal cycle; A: Four probes used for continuous fluid monitoring (temperature, conductivity, pH, and Eh) and chambers for corrosion research and material testing. B: Laboratory autoclave system and coupon mounting system.*

The kits employ vacuum-sealed glass ampoules containing chemical reagents. Breaking the glass tip on the ampoule while the tip is submerged in a process fluid test sample admits a small volume of the sample into the tube, where a chemical reaction occurs, resulting in the development of a characteristic color. The intensity of the color is used to determine the concentration of dissolved gas in the sample, either by using a multi-filter photometer and calibration chart, or directly using a series of comparators.

8.4.14 Pipeline Inspection Tools

The corrosivity of fluids being transported along sub-sea or buried onshore pipelines can be assessed using standard monitoring techniques at accessible locations, which are usually limited to each end of the pipeline. However, detection of localized corrosion of the pipe wall requires the use of intelligent pigs.

There are two principle types of inspection vehicle used to survey the internal and/or external condition of steel transmission pipelines. The first involves the direct measurement of wall thickness by ultrasonics. The second uses an induced magnetic flux in the pipe wall to assess the defect size from the perturbation caused by defects. Both techniques require the pipe internals to be thoroughly cleaned and free of deposits for them to function successfully.

Ultrasonic pigs have the advantage that they measure wall thickness directly. There is also no practical limit to the pipe wall thickness that can be measured and the results are not affected by the proximity of girth welds.

They have the disadvantage that, as with all ultrasonic measurements, a couplant is required between the sensing head and the pipe wall. This means that for successful use in gas lines ultrasonic pigs require to be run in slugs of a couplant such as methanol or glycol, or behind a gel pig.

In older pipelines, where significant internal wastage has occurred, the reliability of ultrasonic pigs is questionable due to the reduced intensity of the reflected signal from the non-planar surface.

Magnetic flux pigs can be run in liquid and gas lines, but rely upon previous wall thickness calibrations taken by direct measurement using ultrasonics, or by reference to pipe manufacturer's data sheets. The maximum wall thickness capabilities for the more sophisticated designs are typically 15 mm for 10 inch ID pipe and 30 mm for 30 inch ID pipe.

The assessment of the material thickness in the weld area is affected by changes in the profile and the thickness of the pipe material, and accuracy is therefore reduced at these locations. In addition, the results are also affected by external welded attachments. For new pipelines a baseline survey should be considered during the precommissioning phase to enable construction defects to be discounted in future surveys.

Surveys using intelligent pigs should be carried out throughout the life of a pipeline. More frequent surveys are to be expected during the early part of the life of a pipeline, becoming less frequent once a level of confidence has been established regarding the corrosivity of the fluids and/or the effectiveness of any corrosion inhibitor treatment program.

Before a pipeline is surveyed using an intelligent pig for the first time, the feasibility of the pipeline for pigging must be assessed. This must include a review of pig launcher and receiver suitabilities and pipeline contours along the full length. A comprehensive cleaning program will normally be essential prior to the survey; for optimum data capture internal gaging may also be justified.

8.4.15 Ultrasonic Thickness Measurement

Conventional compression wave ultrasonics may be used to measure the residual wall thickness in pipework and vessels handling potentially corrosive fluids. The measurement accuracy depends upon the actual wall thickness and the condition of the outer surface of the pipe or vessel in contact with the probe, but will typically be ± 0.5 mm.

Correlations of actual pipe wall wastage can be made with data from the installed intrusive corrosive monitoring devices, but care has to be taken in deriving corrosion rates from ultrasonic wall thickness data in view of the limited accuracy of the technique.

The precise locations on the pipe or vessel being examined should be permanently marked in order to ensure that successive ultrasonic readings are always taken at the same location.

In critical situations, where high corrosion rates are anticipated over a small area, solid coupled probes may be welded directly onto the pipe or vessel at the suspect locations in order to permit continuous monitoring of wall thickness. The proposed welding procedures should be submitted for approval prior to the probe attachment.

One commercial solid coupled probe is available from AGA Technology. Where internal metal loss occurs over a wide area, automated, and manual ultrasonic scanning techniques are available to develop visual displays of the extent and depth of the metal loss.

8.4.16 Radiography

As an alternative to ultrasonics, radiography may be used to examine the internal condition of process pipework and supplement the information on fluid corrosivity received from other monitoring methods. It is particularly useful for the examination of preferential corrosion at weldments and erosion at bends, but the limited accuracy renders it suitable only for the detection of significant changes in pipe wall thickness.

Due to the absorption of the incident radiation by liquids, as well as the pipe wall, its use on-line is limited to small-diameter process streams containing vapors or gases. Under normal circumstances radiography is impractical for examining pipework larger than 8 inches in diameter.

8.4.17 Side Stream Monitoring

Side stream monitoring encompasses the temporary use of a by-pass spool or off-take from the main process stream being monitored to provide supplementary information to that produced by the on-line monitoring devices. Side stream monitoring may be used to examine the short-term effect of chemical additives or process changes upon the electrochemistry of the plant-material–process-fluid system.

The side stream equipment should comprise one or more probe or coupon holder, and flow control and metering devices. It should be used to supplement on-line corrosion monitoring methods and should not be used in isolation, unless on-line methods are not practical.

8.4.18 Visual Inspection

The visual inspection of vessel and equipment internals during periods of plant shut-down should be used to supplement information from on-line corrosion monitoring activities.

8.4.19 Failure Analysis

All plant and equipment failures should be thoroughly investigated, documented, and reviewed in conjunction with the results of on-line corrosion monitoring activities.

8.4.20 Bacterial Methods

In order to measure the propensity for microbial corrosion in a process system it is necessary to quantify both the mobile (planktonic) bacteria and the surface adhering (sessile) bacteria. The mobile bacteria may be enumerated by removing a sample of liquid from the process stream into a clean sterilized container and carrying out a serial dilution test in the laboratory.

The tendency for sessile population development within a system should be assessed by using a bioprobe exposed to the process stream through a standard 5.08 cm (2 inch) high-pressure access fitting. Biofilms may also be removed from standard strip coupons protruding into the process stream.

As bacterial corrosion relies upon the development of bacterial colonies upon the metal surface, it is the determination of sessile populations that is most important in deciding whether or not a problem exists. Bioprobes typically carry six removable studs, on which the biofilms are allowed to develop.

Removal of the studs from the bioprobe enables the growth of sessile populations to be quantified and may provide additional information on the morphology of the corrosion to be expected in the system. Typical exposure times for development of biofilms are two to four weeks.

The corrosion of mild steel as a consequence of the growth of sulfate reducing bacterial populations is characterized by the formation of iron sulfide scale, which can be fairly easily detached to reveal shiny, almost hemispherical confluent pits.

As sessile microbial populations tend to develop predominantly in areas where flow rates are very low, probes should be fitted into deadlegs or other stagnant locations.

The recommended method for examining water samples for evidence of sulfate reducing bacteria in the laboratory is described in API RP 38. In the field, a technique known as serial dilution testing may be used to determine order of magnitude concentrations of mobile microbial populations in water samples.

The serial dilution method uses the same media to culture bacterial populations as does the method described in API RP 38. The technique may be modified slightly to interrogate surface deposits removed from bioprobe studs.

The serial dilution test for a liquid sample is as follows:

1. A sample of water is removed from the process stream into a clean sterilized and stoppered borosilicate glass container. A 1 ml sample of this liquid is introduced into a sterilized syringe and injected into a sealed bottle of a selected culture medium (serial bottle).
2. Following vigorous shaking, a 1 ml sample is taken from the serum bottle and introduced into a second serum bottle using a fresh sterilized syringe. This procedure is repeated with a sample from the second serum bottle introduced into a third bottle, and so on until five serum bottles have been inoculated.
3. The 5 bottles are then incubated at a temperature within 5 °C (41 °F) of the process stream for a 28-day period. Bottles indicating bacterial growth will discolor. The data relating to the concentration of bacteria is dependent upon the number of bottles that have discolored and is reported as the number of colonies over a range from 10/ml to 100 000/ml if a five bottle series is used.

The main drawback with the serial dilution method is the time taken to incubate the colonies. The serial dilution test should be carried out at least twice on each sample of water or surface deposit. More rapid semi-quantitative techniques are available in kit form for detecting bacteria responsible for corrosion, where their presence within a process stream or storage area is suspected.

These techniques are as follows:

- A test using the enzyme hydrogenase is available to measure the activity in the bacterial population. In this test, sulfate reducing bacteria employ the hydrogenase in a microbially induced corrosion reaction. Samples of corrosion product or sludge from bioprobes or the internal surface of the process equipment are exposed to an enzyme extracting solution. After filtering, the enzyme is chemically reduced in an anaerobic chamber. The hydrogenase activity and hence the level of bacteria is assessed by the intensity of color from an indicator dye in the enzyme extracting solution. Results are available within 24 hours. The results obtained from this test cannot be compared directly with results from other test methods.
- Another indirect test measures the bacterial population density by determination of the enzyme adenosphine phosphor sulfate reductase, present in the bacteria. Measurement of this enzyme is again by color intensity, but uses a color interpretation card. The approximate population density can be determined with a detection threshold of 103 sulfate reducing bacteria per ml of liquid sample. Test results can be available within 15 minutes of sampling and show reasonable correlation with those from serial dilution tests.

Enumeration of sessile bacteria begins with the removal of the bacteria from the monitoring stud. This may be accomplished on site by scraping with a scalpel, or by swabbing. A sterile field water solution should be used to collect the removed bacteria for enumeration by one of the above methods.

Sampling for bacterial populations should be accompanied by the following:

- Recording of the date, time, and sampling location
- Measurement of the sample temperature, pH, dissolved oxygen, and H_2S in the sample
- Recording of the concentration of any production chemicals present
- Recording of the appearance of the sample, in particular the presence of slimes, turbidity, color, and smell.

Since bacterial populations may undergo quantitative changes within sample bottles, samples should be analyzed with minimum delay to obtain reliable information.

8.5 Measurement of Dissolved Solids

The measurement of process fluid corrosivity should be supported by measurements of the chemical composition of the different fluid phases present since fluid composition can have an important influence upon corrosion rates, hydrogen damage, stress corrosion cracking, etc.

In aqueous solutions the determination of ions such as $Fe^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Ca^{2+}, Cl^{-}$, $SO_4^{2-}, S2^{-}, CO_3^{-}$ may be carried out by spectrophotometry, colorimetry, or conventional analytical techniques.

The quantitative analysis of non-aqueous samples should be carried out after first ashing the sample in accordance with ASTM D482.

Samples of liquid for analysis shall be taken from the process stream into clean, stoppered borosilicate glass container(s). Reagents should be used so that the ions under test form stable suspensions or complexes. The resulting turbidity or intensity of color change should be determined by photoelectric colorimeter or spectrophotometer and compared to a curve prepared from standard solutions.

Care shall be taken to ensure that other dissolved ions do not interfere with the formation of the suspension(s) or complex(es), giving rise to spurious results.

Detailed test methods and procedures are given in the ASTM Publication "Water and Environmental Technology" Section II, Volumes 01 and 02, and API RP45.

8.6 Measurement of Suspended Solids

The measurement of suspended solids should be carried out where necessary as part of a water quality assessment. In oil-field water injection systems for example, where plugging of a tight formation could result, suspended solids must be kept to a minimum. The measurement may also be used as an indication of deteriorating water quality due to bacterial action and/or corrosion in the system.

The measurement of suspended solids may be undertaken by filter analysis, turbidity meter, or other instruments measuring size and density of particles. Membrane filters are the most suitable for carrying out suspended solids determinations on water that is allowed to flow directly from the process stream.

Methods of determining oil-field water injection quality are described in NACE Standard TM0173.

8.7 Corrosion Product Analysis

The measurement of fluid corrosivity using probes and coupons should be supplemented by the chemical analysis of any corrosion products or deposits that are found, either on the probes and coupons or on the internals of the process equipment during plant inspections.

The following techniques may be used to examine corrosion products.

- Visual examination
- Magnetic examination
- Microscopy
- Wet chemical analysis
- Spectroscopy
- X-ray diffraction and elemental analysis.

The collection, handling, and storage of corrosion products should be in such a manner as to avoid contamination and/or degradation of the sample. Detailed examination should be carried out as soon as possible after removal from the system.

Recommended procedures for the collection and identification of corrosion products are given in NACE Standard RP0173.

8.8 Design Requirements

A corrosion monitoring philosophy should be established based upon a detailed review of the process conditions and plant materials. The potential corrosion problems arising from both routine and non-routine operation of the plant should be assessed in order to determine areas that may be affected. The actual process streams to be monitored and the monitoring devices to be used should be based on this assessment.

8.8.1 Access Fitting Location

As far as practical, access fittings should be installed on horizontal process lines in a vertical aspect. Bottom of the line access fittings show a tendency to accumulate debris that may give unrepresentative monitoring results. It can also result in galling of the threads on the monitoring device and/or the fitting, which could ultimately render the fitting unusable.

Where bottom of the line fittings are unavoidable, flanged access fittings may be used in place of flare weld fittings to enable the fitting to be replaced should problems be encountered. In sour systems, iron sulfide deposits may cause galling problems regardless of the position of the access fitting, and flanged fittings should always be used on such service.

Access fittings should be located a minimum distance of seven pipe diameters downstream and a minimum of three pipe diameters upstream of any changes in flow caused by bends, reducers, valves, orifice plates, thermowells, etc. Where access fittings are installed in pairs there should be a minimum distance of 1 m between each fitting. Where the monitoring devices are intrusive and comprise a probe and a coupon holder, the probe should be located in the upstream fitting to minimize turbulence around the second monitoring device.

The positioning of corrosion monitoring fittings should be such as to allow routine access for probe interrogation and coupon and probe retrieval. Ideally fittings should be located in pipework situated at floor level or immediately adjacent to permanent walkways. The locations of all monitoring points should be marked on the process flow diagrams, materials selection diagrams, and isometric piping drawings.

8.8.2 Access Fitting Design

For operating pressures up to 137 barg (2000 psig) on-line internal monitoring should be undertaken using proprietary high-pressure access fittings that permit the installation and removal of probes and coupons without the need for plant shut-down.

Where on-line retrieval and installation of monitoring devices installed in 2 inch high-pressure access fittings is required, the fittings should be located where adequate clearance is available for installation and operation of a service valve and retriever attached to the access fitting body. The following clearances in Table 8.3 are recommended, based upon the use of fully extended telescopic retrievers.

Table 8.3 *Clearances based on the use of fully extended telescopic retrievers*

Retriever stroke		Clearance (from top of access fitting)	
mm	in	mm	in
660	26	1880	74
860	34	2290	90
1070	42	2670	105
1270	50	3100	122

The required clearance with respect to the outer wall of the pipe in which the fittings are located will be determined by the type of fitting, i.e. flareweld or flanged. For a flareweld fitting the additional clearance will be typically 150 mm (6 inches) and for a flanged fitting 380 mm (15 inches).

Low-pressure access fittings should consist of a weldoflange, a flanged full port valve, a threaded nipple welded into a slip-on flange, and a stuffing box. For this system the maximum recommended operating pressure is 10 barg (146 psig).

The nipple between the valve and the stuffing box should be the same length or longer than the probe element or coupon to facilitate removal of the monitoring device clear of the ball within the valve. The stuffing box should be fitted with a ferrule and locking nut, and chevron PTFE seals. A 25 mm (1 inch) full port valve will normally be large enough to permit the probe or coupon holder to pass freely through the valve body, in fouling duties a 37.5 mm (5.1 inch) valve is recommended.

The exact dimensions of the assembly should always be confirmed before checking that adequate clearance exists. All probes and coupon holders to be used in low-pressure access fittings should be fitted with a blow-out preventer to limit the extent of slide out of the monitoring device through the stuffing box during installation and retrieval operations on-line. Safety clamps should be used with low-pressure access fittings to secure retractable probes and coupon holders while on line.

The maximum operating temperature for each of the two access systems will be governed mainly by the performance of the non-metallic components of the pressure sealing devices utilized within the various parts of the fitting assemblies and probes.

The suitability of the non-metallic seals for pressure containment at the requisite operating temperature should be confirmed prior to procurement.

All high-pressure access fittings should be fitted with heavy duty covers to protect the access fitting threads from damage and contamination. Each cover should have an integral pressure gage and relief valve so that any leaks between access fitting body and the monitoring device can be readily identified.

Sample points for the collection of process fluids for chemical/bacterial analysis should include two isolating valves in series.

8.8.3 Materials Selection

Material selection for access fitting bodies should conform to the requirements of the piping specification for the process line being monitored.

Solid and hollow plugs used in 50 mm high-pressure access fittings should be fabricated from a material that is resistant to corrosion under the process conditions within the line being monitored. In most circumstances Type 316 stainless steel will be suitable, but the final choice should be approved by the company.

The elastomeric components used for pressure sealing should be demonstrated to have satisfactory performance in the expected process fluids.

Access fittings should be welded onto the process pipework in accordance with approved welding procedures. The inspection and testing of the attached fitting should comply with the appropriate piping fabrication code. On successful completion of the pressure test the access hold should be cut in the pipe wall centrally within the access fitting using a 38 mm (1 3/8 inch) milling cutter. Proprietary drilling machines mounted on the access fitting may be used for this purpose. The flame cutting of access holes prior to the attachment of the fitting is not permitted.

8.9 Automated Systems

Methods for the interrogation of corrosion probes range from hand-held analog or digital meters to multi-channel dataloggers linked directly to microprocessor-driven data analysis units. The selection of the data collection method is governed by the following considerations:

- The number, range and distribution of corrosion monitoring devices
- The required frequency of data collection
- The availability of manpower for data retrieval
- A comparison of the capital and operating costs associated with the various options.

8.9.1 Manual Methods

Hand-held instruments for the interrogation of corrosion probes range in versatility from simple direct reading meters dedicated to one probe type and with no data storage facility, to multi-function meters with direct readout, data storage and retrieval, and computer interface capabilities for optimum data recording and data analysis.

Rack-mounted instruments providing direct analog or digital readouts of the corrosivity readings from a number of probes are also available.

8.9.2 Data Loggers/Collection Units

Data logging instruments hard-wired to the monitoring devices may be single or multi-channel. Single-channel instruments have the advantage that they may be mounted local to the monitoring point to minimize the length of the cable run.

Removable memory modules allow manual transfer of the recorded data to the office, where it is downloaded to a personal computer for interrogation.

8.9.3 Transmitter Units

Individual or multi-probe transmitter units are available that are mounted local to the probe and used to receive, process, and transmit the probe signals to a remote interrogation unit. The interrogation unit may be either a dedicated chart recorder, a digital display unit or a process computer.

8.9.4 Computers

Computers dedicated to corrosion monitoring may be used to receive data from corrosion probes, either via transmitter units or multiplexers. The computer facilities enable selection of recording

frequency and alarm setting. Sequential scanning through the active channels provides a display of "real time" probe values. They are primarily concerned with data collection and display, and data storage capabilities vary according to manufacturer, but are generally limited. Further data analysis and permanent storage of data is catered for by interfacing with a personal computer, programmed using dedicated software.

8.9.5 Data Analysis and Reporting

The methods used to analyze the corrosion monitoring data will be determined by the number, location, and variation in monitoring devices used and the method of data collection.

Suitable computer software may be available commercially for this purpose or may be modified to suit the particular application. In selecting computer software consideration should be given to the inclusion of plant process data and plant inspection results.

The frequency and format of reporting the results should be determined by the company corrosion engineer. The reports should make reference to significant processing parameters and any chemical treatment programs carried out during the time interval covered, and highlight any significant change in fluid corrosivity. Detailed corrosion monitoring reports should be issued annually, but may be required more frequently where on-line monitoring is used to assist in plant control.

8.9.6 Guidelines for Safe On-Line Installation and Retrieval of Corrosion Monitoring Devices

8.9.6.1 Low-Pressure Systems

- Probe/coupon removal procedure:

1. Loosen and remove the nuts holding the upper safety clamp plate. Remove the plate, taking care to ensure that the safety clamp rods are supported.
2. Loosen the ferrule locking nut, taking care in case the probe or coupon holder stem is forced up through the packing gland assembly by the line pressure.
3. Slide the probe or coupon holder stem out through the packing gland assembly until the probe element or coupons clear the valve ball or gate. There should be a mark or label on the stem to indicate when this position has been reached.
4. Close the valve.
5. Slowly release the pressure contained within the assembly above the valve by loosening the bolts on the upper flange of the valve.
6. Remove the bolts from the upper flange on the valve and lift off the flanged nipple, clamp, and packing gland assembly with the probe or coupon holder.
7. Fully withdraw the probe or coupon holder from the packing gland. Complete removal of coupon holders may not be necessary. The coupons may be removed, the holder cleaned, and new coupons fitted with the packing gland, etc. still in place.

- Probe/coupon installation procedure:

1. Slide the coupon holder or probe stem through the flanged nipple and into the stuffing box, having first checked that the bottom plate of the safety clamp is in place around the nipple. If this is not the case then the nipple and packing along the assembly will need to be split, the plate fitted, and the two reconnected.
2. Adjust the position of the probe or coupon holder so that the bottom of the probe element or the coupons will be clear of the valve ball or gate when the assembly is in place above the

valve. Mark the stem of the probe or coupon holder where it emerges from the top of the ferrule locking nut to record the "clear of the valve" position.
3. Check that the flange faces on the flanged nipple and upper valve flange are clean and the gasket in good condition.
4. Mount the assembly on top of the valve and bolt up the mating flanges securely.
5. Partially open the valve and check for leaks. If a leak is evident at the top of the packing gland, tighten the packing retaining nut until the leak stops.
6. Once the assembly is leak free, open the valve fully and slide the probe or coupon holder through the valve and into the process stream. The distance of travel of the probe should be checked to ensure that the monitoring position is correct and that the probe element or coupons are not damaged by contact with the opposite wall of the pipe.
7. Where coupons are being installed, ensure that they are correctly orientated parallel with the direction of flow of the process stream.
8. Tighten the ferrule locking nut securely with a wrench or spanner, while preventing the packing retaining nut from moving with a second tool.
9. Assemble the safety clamp, ensuring that the upper clamp plate fits securely over the top end of the probe or coupon holder and prevents any upward movement of the same.

8.9.6.2 High-Pressure Systems

The following constitutes guidelines for the installation and retrieval of on-line corrosion monitoring devices using a high-pressure telescopic retriever and pressure test valve. On-line retrieval/installation of corrosion monitoring devices should only be carried out by operators skilled in the use of the equipment. The owner of retrieval tools and service valves used in retrieval operations should be in possession of valid certificates confirming that tests have been carried out that demonstrate that the equipment is suitable for the pressures and temperatures at which it will be used.

- Valve integrity test: Fittings without integral service valve installed

1. If a pressure gage is fitted, check and note the pressure gage reading. Bleed off any pressure and monitor the rate of subsequent pressure build-up. Notify the plant operator if there is a significant leak on the fitting and abort the retrieval operation. Where no pressure gage is fitted, gradually remove the threaded heavy duty cover from the fitting, carefully noting any obvious leakage. Notify the plant operator if there is evidence of significant leakage and abort the retrieval operation, replacing the cover. Where no leakage is found, remove the cover completely, clean the access fitting threads and install the service valve.
2. Install the retrieval tool; pressure up the entire assembly with the service valve open to 110% line pressure. This checks the connection between the service valve and the access fitting.
3. Close the service valve, depressurize, and remove the retrieval tool, keeping the service valve closed.
4. Check that the service valve is not passing, if nitrogen is used as the test medium, use soap solution to check for leaks.
5. If no leakage is observed, bleed off the pressure using the by-pass valve.

- Valve integrity test: Fittings with integral service valve installed

1. Remove the threaded heavy duty cover and clean the threads. Check the integrity of the plug fitting by cracking open the by-pass valve.
2. Install the retrieval tool and pressure up the entire assembly with the service valve open (to 110% line pressure).

3. Close the service valve; depressurize and remove the retrieval tool, keeping the service valve closed.
4. Check that the service valve is not passing, if nitrogen is used as the test medium use soap solution to check for leaks.
5. If no leakage is observed bleed off the pressure using the by-pass valve. If leakage is observed, suspend operations.

- Coupon/probe retrieval

1. Make up the retrieval tool to the service valve and open the service valve.
2. Pressure test the entire assembly to 110% line pressure.
3. Engage the retriever mandrel in the plug fitting.
4. Back-off the plug until a small product bleed is observed, allow pressure in the retriever to equalize to line pressure.
5. Unscrew the plug completely and withdraw into the retriever body.
6. Close the service valve (ensure mandrel is clear of valve).
7. Remove the retrieval tool and change out the probe/coupon as required.

- Coupon/probe installation

1. Make up the retrieval tool (with the probe/coupon holder installed) to the service valve.
2. Pressurize the tool to 100% line pressure. Check for leaks.
3. Crack open the by-pass valve to allow line pressure into the retrieval tool. Allow pressure to stabilize and check for leaks.
4. Fully open the service valve.
5. Insert the probe/coupon holder into the fitting and screw home.
6. Depressurize the retrieval tool and check for any pressure build-up. This checks the integrity of the plug seal.
7. Disengage the tool from the plug.
8. Remove the retrieval tool – ensure pressure is zero. Note: If coupons are being installed, their final orientation may have to be adjusted at this stage, use the retrieval tool or a socket wrench.
9. Clean the plug top, service valve, etc. and replace the threaded cover. On completion, the retrieval tool should be stripped down, cleaned, and re-greased prior to storage.

8.10 Evaluation of Corrosion Inhibitors

In order to determine the effect of chemical additives on corrosion, an actual corrosion process must be taking place, so that the inhibitor test and the corrosion test are inseparable. The fact that many variables affect a corrosion process means that numerous different inhibitor tests are available. Although additive concentration is generally low, the type of system, whether once-through or recirculating, or the method of treatment, continuous or batch-wise, will determine, not only the test method, but also the inhibitor concentration required.

8.10.1 Reasons for Inhibitor Testing

Inhibitors may be tested in many ways or for different reasons, but basically, the objective is to determine the effectiveness of a chemical additive in slowing down the overall corrosion process. Evaluation of new additives is necessary as chemicals are developed for new systems or for existing applications. Then, when an inhibitor looks promising or is ready for field use, it is necessary to judge its performance under field conditions.

Associated with the effectiveness of an inhibitor, however, are other inherent properties necessary to carry it to the metal surface where it does its job. These properties often directly contrary to properties considered ideal for corrosion inhibitors, also must be included in an evaluation.

It is the purpose of this section to describe the variables that affect the properties and performance of an inhibitor, and the tools and techniques necessary to measure them, both in the relatively controllable conditions of a laboratory and in the practical, usually more difficult conditions in the field.

8.10.2 Inhibitor Properties

Desirable properties of a corrosion inhibitor formulation include:

- that the formulation stifle or reduce the corrosion process,
- that transport of the active ingredient to the metal surface be promoted,
- that no undesired side effect results.

Because effectiveness, as well as many other physical properties, must be considered for each application, evaluation may involve many unrelated tests.

The inhibitor may interfere with either the anodic or the cathodic reaction. The effect of inhibitor on the corrosion rate is essentially a measure of the integrity or tightness of the barrier formed on the metal surface. In an evaluation for effectiveness, one is interested in the integrity or tightness of the barrier and the amount of additive necessary to form it.

In certain cases, when inhibitors are applied batchwise, the tenacity or permanence of the barrier film is important. This property is called persistency. Persistency involves a time factor; it is a measure of time between batch additions over which the inhibitor maintains a protective barrier in the uninhibited environment.

Inhibitor concentrations vary from a few parts per million in continuous injection applications, to several thousand parts per million in closed systems, to batch treatments of the "neat" or undiluted inhibitor. Concentrations used influence test conditions and often determine whether or not undesirable side effects are encountered.

The relationship between additive concentration and corrosion rate raises the question of just what can be accomplished in reducing corrosion. Should complete stifling of corrosion be the goal? If some small amount of corrosion is acceptable, is this then in the form of increased pitting, compared to the untreated system, thus making the situation worse than without the inhibitor? This consideration is particularly important when working with anodic-type inhibitors such as chromate.

8.10.3 Test Conditions

Before undertaking a program of evaluating inhibitors for effectiveness in mitigating corrosion, one must review the overall problem and determine what is required of the inhibitor, that is, exactly what parameters are to be tested and what factors affect test results. These questions and their answers will help in obtaining meaningful data for selection of the most efficient inhibitor in the environment of interest. The first step is to select the critical environmental conditions of interest and to incorporate them in the test.

If the corrosion problem is stress cracking, it is of little value to design a test that mainly involves general corrosion. Unfortunately, many tests consider only the overall loss of metal, a measure of uniform corrosion, and attempt to read into the data information that cannot be or is not measured.

In designing a laboratory test, it is important to simulate physical field conditions and to select corrodent(s) important to the field conditions. Some important corrodents dissolved in aqueous systems are listed below (in some cases, combinations of these will be common):

- Oxygen
- Carbon dioxide
- Hydrogen sulfide
- Ammonia
- Acids, bases
- Acid salts
- Oxidizing agents
- Dissolved solids and scale formers.

The physical parameters of the test include the following:

- Temperature
- Pressure
- Velocity or agitation
- Surface-to-volume ratio
- Dual phase immersion
- Presence immersion
- Presence of crevices
- Presence of stresses.

Since the corrosion process directly involves a metal, the mechanical and metallurgical properties of the metal are important. The content of alloying or secondary constituents, heat treatment, and method of forming determine the characteristics of the metal. If stress is involved, one must keep in mind the applied and residual stress, as well as the effect of notches as stress raisers.

If more than one metal is involved, galvanic corrosion is a possibility and the ratio of areas of the metals will dictate intensity of attack on the anodic metal. Surface preparation of the specimens may be effected in different ways.

Some investigators sandblast coupons, while others polish them with 400 grit or other abrasives. In any case, the surface of the metal must be clean, uniform, reproducible, and oil-free, so that meaningful corrosion results may be obtained. This is necessary, even though the condition of the metal surface may not be typical of metals exposed under field conditions.

8.11 Detection of Corrosion

One of the most important aspects of an inhibitor test is the actual measurement of changes that reflect the degree of corrosion. In all cases, the metal of interest comprises the specimen, but the actual changes measured may not necessarily involve the metal directly:

- Measurements directly related to actual metal loss occurring during the corrosion process
- Measurements utilizing a related part of the overall electrochemical corrosion process
- Measurements not involved in the electrochemical process, such as time, or surface film thickness.

8.11.1 Methods Involving Loss of metal

Most direct measurements of corrosion utilize the weight loss of metal over a period of time on a small sample such as a coupon, wire, or strip. The dimensions of the coupon are important for several reasons. The ratio of surface area to coupon weight should be as high as possible to facilitate detection of small weight losses. This permits the shortest possible exposure period between weightings. Selection of the maximum surface-to-weight ratio, however, may still result in a relatively long test.

A long time between weightings is disadvantageous because it averages weight loss over the interval so rate of attack fluctuations are missed. However, a large specimen has the advantage of being able to detect and measure pitting attack. Thus, in many cases, the coupon weight loss method must be a compromise between the length of test, the sensitivity of the weight measurements, and the importance of observing pitting corrosion.

The coupon technique is by far the most common and most inexpensive method in current use. The preparation of coupons is discussed in some texts in general terms, and some standards have been set up for specific tests.

A standard coupon that may be used for many inhibitor test programs is scheduled to be issued by NACE Committee T-3-P. This coupon, developed by and used for many years by NACE Committees in testing inhibitors in products pipelines has the advantages of being made of homogeneous material of specific analysis, uniform surface preparation, and controlled size and weight. Reproducibility of either static or dynamic tests can be improved by using this coupon and it is especially valuable when comparisons need to be made among results achieved by several different laboratories.

The disadvantage of lengthy test times has been decreased by the development of the Corrosometer, a device that measures metal loss directly in periods as short as one hour. The Corrosometer detects the change in electrical resistance of a small specimen resulting from loss of metal. Another advantage of the Corrosometer is that the electrical measurements can be made while the specimen is in place, without disturbing the system or the corrosion products. The Corrosometer technique can be used in aqueous liquids, non-aqueous liquids, and gaseous or solid systems. Because specimens are small, pitting is not always detected and if the specimen does pit, instrument response is not linear with respect to the metal lost.

The analytical measurement of iron or other soluble metal content in the corrodent stream is another method directly related to metal loss. This technique can give poor results if the corrosion products are insoluble or adherent to the metal surface. If the method is used in a two-phase system, either both phases must be analyzed for metal ions, or particular care must be taken to put the dissolved metal into the aqueous phase. Quantitative measurements of dissolved metals are used frequently in acidic systems or in special cases where the corrosion products are known to be soluble. There are inexpensive colorimetric tests available for measuring iron, copper, and other metals in solution.

8.11.2 Indirect Measurements for Corrosion Detection

Indirect methods of corrosion rate measurement involve aspects of the electrochemical process other than metal dissolution. These measurements involve cathodic reactions, such as the evolution of hydrogen, or consider current–potential relationships, such as polarization curves or polarization resistance values.

8.11.2.1 Hydrogen Evolution

Hydrogen evolution can be used where reduction of hydrogen ions is the cathodic reaction, e.g. in acidic solutions. The method can be cumbersome, because the solubility of hydrogen in the solution and hydrogen absorption into metals must be considered. The method is most practical at high rates of corrosion in acids, but is not too commonly used. In one case, the technique has been used for rapid screening of acid inhibitors.

An interesting variation of the hydrogen evolution technique is that in which hydrogen from corrosion enters the steel and is then measured. The build-up of hydrogen pressure in a “volume-less cell” is a measure of potential hydrogen blistering that may be caused by certain environments containing chemicals such as sulfides or cyanides that interfere with the normal evolution of molecular hydrogen and make it enter the metal in atomic form.

The environment may be either acidic or basic. A technique using the effects of diffused hydrogen on current flow between electrodes in a vacuum has been used to study corrosion mechanisms and should be valuable for inhibitor studies, because the sensitivity of this method is considerably better than that of the pressure build-up technique.

8.11.2.2 Current–Voltage Relationships

Current-voltage relationships are commonly used as measurements of corrosion and are consequently of value in evaluating inhibitors. The first determines the potential versus current curves for both the anodic and cathodic reactions. Data are plotted on a semi-logarithmic current scale and are extrapolated backward toward the low current direction until the anodic and cathodic curves intersect, the current density at that point representing the rate of corrosion.

The second method uses polarization resistance, which is the slope of the polarization curves at the point of corrosion. This method has practical use both in the laboratory and in the field.

Instruments for polarization-resistance-type corrosion measurements are commercially available as the "Corrater" and the "Pairmeter." The instruments translate polarization resistance data into corrosion rates and are known as instantaneous corrosion-rate meters. The polarization resistance method is also reviewed in an NACE Task Group report, with a complete bibliography.

Another type of rate meter is one that uses the complete electrochemical circuit in the form of a galvanic cell. While the galvanic cell may not simulate the actual corrosion cell, it does generate its own current and voltage; the cathodic and anodic reactants can be the same as those of the corrosion cell and the current generated is proportional to the corrosion rate. This system forms an inexpensive qualitative instrument for field use and can be used to monitor and evaluate corrosion inhibitors.

Instantaneous corrosion rate meters all have the advantages of detecting very rapid changes in the rate of corrosion without disturbing the corrosion process. The measurements can be made at locations distant from the location of the electrodes. A disadvantage, as with all current–voltage methods, is that the measurements must be taken in a liquid, aqueous phase that has a reasonable electrical conductivity.

8.11.3 Utilization of Film Measurements

A relatively new method of inhibitor evaluation directly measures film thickness on the metal surface by a technique known as ellipsometry. This method is an optical one, in which a change in the character of a polarized light beam reflected from a surface is used to measure film thickness.

Refined equipment is necessary to generate and measure the reflected light beam. Surface conditions are also critical. Although this may be an interesting tool for mechanistic studies in the laboratory, it is not presently useful for rapid laboratory or field evaluation if inhibitors.

Similar methods directly related to surface films are involved in "double-layer capacitance," "differential capacitance," and "nuclear magnetic resonance" techniques, described in the recent literature. As with ellipsometry, advantages are sensitivity in measurement, but equipment requirements limit these techniques to laboratory use, and therefore are mostly for highly theoretical, mechanistic studies.

The copper ion displacement test is another method that measures directly the barrier effect of an inhibitor film. In this technique, steel coupons are immersed in the inhibited solution to develop a protective film formed under the conditions of the environment. Then on a "go/no-go" basis, the coupon is removed and immersed in an acidified copper sulfate solution.

If the inhibitor film is not protective, copper plates out on the steel surface and is readily seen. The method has some disadvantages in that the inhibitor film must be resistant to the acid conditions of the plating solution, and that correlations for each particular environment should be checked.

One evaluation of the method indicates that it works well under strong filming conditions where hydrogen sulfide is present, but does not work well in a carbon dioxide environment. The method has been used as a laboratory screening test for determining inhibitor persistence. When the method is applicable, it can be a useful tool for field evaluation of inhibitor treatment.

The last method in which the adsorbed film is involved is one in which tagged radioactive molecules expose photographic film and reveal a "picture" of the areas they cover. The technique is qualitative and may be useful for laboratory studies. In a more practical vein, radioactively tagged molecules can also be a very useful field tool. This technique has been used to measure areas covered by an inhibitor and the inhibitor persistency time.

8.12 Miscellaneous Corrosion Tests

Several tests are not related to any particular part of the corrosion process, but involve only a specific test specimen that responds to corrosion by complete failure. These tests are used in the measurement of certain forms of corrosion involving factors such as stress. Examples are: corrosion fatigue, stress corrosion cracking, and hydrogen embrittlement. In designing such corrosion tests, the variety of test specimens parallels the number of applications.

Stress corrosion tests may use a constant applied stress or one that changes as the crack progresses. Corrosion fatigue tests may vary in the way cyclical stresses are applied: tensile only, or tension-compression.

The commonly used test for caustic embrittlement employs an applied stress along with a technique to concentrate dissolved solids at the critical area. When complete failure of the specimen is involved (e.g. breaking), the measured variables can be:

- time to failure
- stress to cause failure
- concentration of the corrodent to cause failure, all other variables being held constant.

In summary, any corrosion test can be used to evaluate corrosion inhibitors, as long as it detects a difference in corrosion with and without the inhibitor. The most meaningful test is one that closely simulates field conditions. Sensitivity of measurements may not always produce the most useful results and requirements of the test method can vary widely depending on whether it is used in the laboratory or in the field.

8.13 Results of the Test Method

Despite strenuous efforts, duplicating field conditions may be difficult or impossible, this objective being subject to the additional difficulty that conditions actually are unknown. Many times, an evaluation test may be altered to develop a more corrosive condition or to "accelerate" the test.

In such cases, the combination of corrodents should remain the same, but it may be necessary to increase concentrations. The question then arises concerning interpretation of data. If the test is accelerated, the absolute corrosion rates may be higher than those resulting under field conditions.

However, it must be assumed that the same corrosion mechanism is taking place and if an inhibitor is effective at high corrosion rates, it will also be effective under milder conditions. Testing using comparative data under accelerated conditions will permit identification of the better inhibitors. Then, under field conditions, the actual dosage of the inhibitor may have to be determined in some other manner.

In a laboratory test, the question always arises as to when an inhibitor is effective. Must the corrosion rate be stopped completely or can it be slowed to some degree and still be effective? In the field, the decisive factor will be whether the inhibitor eliminates failures.

A complicating factor in both laboratory and field is the fact that corrosion products (or other surface-active particles) will adsorb the inhibitor and either keep it from the metal surface or lower its available concentration. Still another factor to consider in interpreting data is the wide statistical band over which test results will vary until a minimum necessary concentration of inhibitor is exceeded.

Quite often, the individual test method, while stimulating field conditions accurately, will not give reproducible results because of variables such as surface preparation, velocity and adsorption of inhibitors on solid particles, and other factors, some of which are indeterminate. Several investigators have reported the use of statistical methods in the evaluation of test results.

8.14 Field Testing of Inhibitors

The most reliable test apparatus is field equipment itself. However, it is the most expensive because of the cost of the equipment and because testing in full-scale equipment is time consuming.

No source of information should be ignored, though, in evaluating additives or process variables, and much valuable data can be obtained if careful day-to-day records are kept on equipment performance. A simple tabulation of failures versus time can show improvements resulting from inhibitor treatment. The records can be made even more sophisticated by identifying various parts of the equipment that fail and by deciding whether wear, stresses, or other factors have been involved.

A method of record keeping that has been used in treated water systems is to plot the logarithm of cumulative leaks against time. A plot of this type will approximate a straight line, indicating that the number of leaks increases with time. As a treatment becomes effective, the slope of such a line will be reduced.

Field testing usually is performed by means of coupons exposed to the test environment. The coupons can be installed on a holder in the full flow of a process line of interest. Another method is to use a test pipe nipple in the flow line to simulate more closely velocity conditions.

When either of these techniques is used, however, inhibitor treatment of the complete stream is necessary for the relatively long times needed for coupon exposure. To minimize the test times, electrical resistance probes, polarization resistance electrodes, or iron counts can be used, when applicable, reducing test times to days instead of weeks.

A further refinement is to use a slip stream off of the actual process lines. In this method, small amounts of the actual process fluids are passed over the metal specimen so only small amounts of inhibitors are needed for evaluation. If electrical resistance probes or polarization resistance electrodes are used, many additives can be checked in a short time.

8.14.1 Illustrations of Complex Testing Procedures Necessary to Simulate Field Conditions

An inhibitor evaluation test often will involve more than merely exposing a sample of metal to a corrosive environment. In this sub-section, four laboratory tests will be described to illustrate the complex conditions or the specific properties that can be encountered in designing a test to meet certain applications. Table 8.4 summarizes the conditions of each of the four tests and the other requirements peculiar to the application. Tests are also discussed below in detail to elaborate on the reasons that make them different from others.

Table 8.4 *Summary of conditions and specific requirements of four different test examples*

	1	2	3	4
Reference to standard tests	Anti-freeze for Internal Combustion Engine ASTM D1884, D2570, D1881, D1121	Clear Packer Fluidfor Annulus of Oil or Gas Wells Bottle Tests for Solubility and Compatibility	"Wheel Test" Alternate Immersionfor Two-Phase Systems Bottle Tests ASTM D1935, D2550	Recirculating Water for Cooling Towers ASTM D2688,D2776
Environment	Water and freeze point depressant: - Low dissolved solids - Air-saturated - 71 °C to 82 °C - Agitated	Brine, weighted with high concentration of NaCl, $CaCl_2$ or $ZnCl_2$: - De-aerated - Contaminated with H_2S or CO_2 - 66 °C to 177 °C - Static	Two phases hydrocarbon may have high or low viscosity, may contain straight chains or aromatics, quite often taken from field installation. Aqueous phase may have high or low dissolved solids.: - Saturated with air, CO_2 or H_2S - Ambient to 93 °C - Mild agitation	Water, with moderate dissolved solids: - Air-saturated - 49 °C to 60 °C - Agitated
Metal of interest	Steel, Al, Cu, brass, cast iron	Steel	Steel	Steel, Cu alloys
Specific requirements	1. Galvanic coupling 2. Reserve alkalinity 3. No foaming 4. High surface-to-volume ratio	1. Solubility at elevated temp. 2. High surface-to-volume ratio 3. No reaction with CO_2 or H_2S 4. Compatibility with bactericides	1. Solubility 2. Dispersibility 3. Water tolerance in oil 4. Detergency 5. Foaming 6. Compatibility with other additives 7. Pour point	1. Heat transfer 2. Compatibility with other additives 3. Non-polluting 4. Non-foaming
Method of detection	Coupon galvanic current	Coupon	Coupon Corrosometer Polarization resistance	Heat exchanger Coupon (tube)

8.14.1.1 Anti-Freeze for Internal Combustion Engines

The cooling system for an internal combustion engine contains a variety of metals, plastics, and rubber in contact with the aqueous coolant. The coolant has a relatively low volume for the area contacted and remains essentially unaltered, except for makeup over a period of one to five years depending on the maintenance program. An additive must not accelerate degradation of any of the structural materials in the cooling system.

The principal corrodents are oxygen from the atmosphere and hydrogen ions from degradation of ethylene glycol, commonly used as an anti-freeze. Because the system contains a minimum of dissolved chlorides and sulfates, this minimizes the problem of corrosion and the requirements of the inhibitor. In time, however, as makeup water is added, dissolved solids will increase in concentration.

The main requirement of a test to evaluate inhibitors for such systems is providing several representative galvanic couples exposed in an aerated, hot, agitated mixture of water and anti-freeze. The ASTM D1384 test describes the method, solution composition, and coupon size and coupling for a glassware test. Steel, cast iron, aluminum, solder, brass, and copper coupons are galvanically coupled in the test method. Another paper describes a test procedure on several common inhibitors and their effectiveness on the various individual metals and galvanic couples.

Other properties of the inhibitor formulation are important to insure optimum performance of the coolant. Foaming should be prevented so heat transfer is not impeded in any part of the engine. The ASTM D-1881 test describes a technique for evaluation of foaming characteristics.

Reserve alkalinity is a property required to provide a reasonably long period of constant pH conditions. Degradation of glycol anti-freezes can lower the pH to the acid range. The ASTM D-1121 test describes a method for determining reserve alkalinity of an anti-freeze formulation.

8.14.1.2 Clear Packer Fluids for the Annulus of an Oil or Gas Well

The packer fluid system, similar to the automotive coolant, contains a large area of metal in relation to the volume of fluid. However, the system differs in that the packer fluid is de-aerated, static, and contains a high concentration of dissolved solids.

The evaluation test requires a static system with the proper surface-to-volume ratio. Since the required temperature is high and air must be eliminated, a pressurized bomb with a glass liner makes a suitable test vessel. Because a relatively large area is needed, coupons are the simplest and most logical detection technique, although others can be used.

The deficiency of the test is that uniform corrosion is measured, even though localized pitting is quite often the mode of failure in oil or gas well tubing. However, because of its large area, the coupon can be inspected for pitting. Because the de-aerated system alone does not produce a very high uninhibited corrosion rate, in this case an accelerated test is achieved by adding carbon dioxide or hydrogen sulfide to the system.

Organic inhibitors are often used in a packer fluid at high concentrations, so solubility becomes a problem. Solubility tests must be carried out at an elevated temperature because some organic inhibitors become less soluble as temperature is increased. The pH value at a high concentration should be checked because some highly soluble formulations are acidic. Furthermore, other additives such as bactericides often are included in the packer fluid system, so compatibility tests also must be considered.

8.14.1.3 "Wheel Test" Alternate Immersion in Two Mutually Insoluble Phases

Contacting the metal specimen with the proper mixture and for the proper time in each phase is difficult in laboratory testing, particularly when the inhibitor may have preferential solubility in one of the phases.

The aqueous phase can be either a condensate, such as exists in fuel product pipelines, or it can contain moderate amounts of solids, such as is the case in refinery crude distillation overheads, or it can be strong brine, as in the aqueous phase produced in an oil well. The hydrocarbon phase can vary among aromatic, aliphatic, saturated, and unsaturated compounds, all of which can affect the solubility and the effectiveness of the inhibitor. Both fluids may be saturated with gases, such as carbon dioxide, hydrogen sulfide or air that will be factors in determining corrosiveness and the requirements of the inhibitor. Temperatures may range between ambient and 205 °C (400 °F).

Because a dual-phase system may be treated with an inhibitor continuously or batchwise, the properties of the inhibitor should be selected to correspond with the treatment method.

The "wheel test," however, measures only the actual effectiveness of the inhibitor in minimizing corrosion. Persistency (long-term effectiveness by a strongly adsorbed film in an uninhibited environment) and solubility determinations are supplementary tests used to evaluate desirable properties for the batch treatment method.

Although the "wheel test" is used sometimes in persistency testing, care must be taken to minimize an increase in inhibitor concentration in the uninhibited fluids through carryover from the treated metal sample. A good review of this method and its results is given in a report of a cooperative test carried out by an NACE Task Group T-ID-2 on evaluation of film persistency.

The "wheel test" attempts to simulate the time and frequency of specimen immersion in both phases of the dual system. Exposure to both phases is accomplished either by rotating or by oscillating bottles containing the fluids and metal specimen. With the coupons or electrodes at one end of the bottle, the heavier aqueous phase will cover the specimen once in every cycle.

The frequency of rotation or oscillation determines the time in each phase and the degree of agitation in the system. When the rotating bottle assembly is installed in an oven to provide elevated temperatures, it is installed in an oven to provide elevated temperatures, it is necessary to use vessels capable of withstanding pressure.

The total volume and the ratio of the two phases must be taken into account for two reasons:

1. Determination of inhibitor concentration.
2. Effects of corrosion products.

If the inhibitor is soluble in only one phase, the effective concentration can be determined directly. However, if the inhibitor distributes itself between the two phases, the relative volumes, as well as the distribution coefficient will determine the concentration in each of the phases. The amount of corrodent in the aqueous phase will determine changes occurring in soluble and/or insoluble products as a result of corrosion.

If corrosion is completely stifled by the inhibitor there will be no changes. However, the formation of either soluble or insoluble corrosion products and the depletion of the corrodent can change the corrosivity of the aqueous phase, particularly if this phase has a small volume. Insoluble corrosion products also can provide a large surface area on which the inhibitor can adsorb, thus depleting the inhibitor available to the metal.

The "wheel test" requires two phases closely approximating the actual environment of interest (the actual fluids, if possible), and a clean specimen of metal in the form of coupons, Corrater electrodes or Corrosometer probes. Use of the Corrater or Corrosometer permits the use of prerusted surfaces if these are necessary in the evaluation of the inhibitor.

The inhibitor is added before the metal contacts either phase and in some cases, the metal specimen is soaked for a short period in the inhibited hydrocarbon phase prior to alternate immersion. Quite

often, the test is accelerated by saturating the fluids with carbon dioxide or hydrogen sulfide, using a much higher concentration of the acid gases than is encountered in the field.

While the use of Corrater electrodes and Corrosometer probes in laboratory testing is described in the literature, these sensing methods are more useful under field conditions, where rapid evaluation in the actual environment is desired, rather than laboratory testing under accelerated conditions.

Because of the wide variety of two-phase systems and because of the potential problems related to inhibitor treatment, other properties of the inhibitor formulation become quite important; each application will have its specific problems and requirements. Inhibitor solubility is an important factor and usually will be dictated by the major phase present.

In certain cases, such as in batch treatment of oil wells, dispersibility of an oil-soluble inhibitor into an aqueous phase is necessary merely to carry the inhibitor throughout the system. Dispersibility is also necessary for the same reason when using the relatively insoluble inhibitors for long-term persistency in batchwise treatment.

In most applications involving dual-phase systems, inhibition against corrosion is only one of the problems. Anti-scale inhibitors, bactericides, or other additives may be added along with the inhibitors. In such cases, supplementary tests must be carried out to determine their mutual interaction. The different chemicals may be synergistic in their desired effects, but most likely they will interfere with each other.

8.14.1.4 Recirculating Cooling Water Test

The surface-to-volume ratio is relatively low in such systems so that little effect on the bulk fluid can be expected from the corrosion process. In many cases, metals other than carbon steel are used for heat exchanger tubing, including Admiralty brass, cupronickel, stainless steels and to some extent, aluminum and titanium.

8.15 Inhibitor Properties Other Than Effectiveness in Mitigating Corrosion

In many applications, properties of the inhibitor other than its effectiveness in inhibition are equally important in obtaining maximum efficiency with a minimum of undesirable side effects. Some of these properties have been discussed in previous sections, illustrating the importance of solubility, compatibility, portability, and other characteristics in the four examples of inhibitor evaluation.

In this section, the properties listed in Table 8.5 will be discussed, showing their relationship to inhibitor effectiveness or their undesirable side effects on the system. When known, a method of evaluating the property of interest will be described.

The properties of the "neat" inhibitor formulation (i.e. as received from the formulators) are important mainly from the standpoint of handling the material. Low viscosity is necessary to provide adequate pumping rates or flow rates. For example, when an oil well is treated batchwise, the time to reach the bottom and the hang-up on the surfaces depends on viscosity, which accordingly affects the shut-in period. Downtime costs money.

Often, the inhibitor may be diluted just prior to injection to improve its mobility. Pour point is related to viscosity and is mainly important during cold weather. The inhibitor must flow at the lowest temperature expected at the location of use. Often the active ingredient of an inhibitor formulation is only 20% of the bulk, in order that the proper viscosity and pour point can be achieved through dilution.

Table 8.5 *Important properties of inhibitor formulation other than effectiveness in mitigating corrosion*

	Broad classification	Specific property of interest	Test method
1	Property of neat inhibitor formulation	Viscosity Pour point Density	ASTM D2162 and D88 ASTM D97 ASTM D1217 and D1298
2	Effect of mixing with environment of interest	Solubility Water tolerance Emulsion formation Foam formation	Bottle tests ASTM D2550 ASTM D1935 and bottle tests ASTM D1881
3	Reactions with other additives	Compatibility with: • bactericides • scale inhibitors • dispersants	Bottle tests Effectiveness tests
4	Effect on animal life	Portability	Tests not within scope of this chapter. See government regulations covering specific material.
5	Miscellaneous effects of temperature	Drying Solubility changes Release of Weighted Inhibitors	Drops applied to hot plate Bottle Tests Bottle Tests

8.15.1 Influence of Density

Density is important in achieving proper mixing of the inhibitor in the corroding stream. High-density inhibitors have been developed for batch treating a two-phase system, such as an oil well, where getting the inhibitor to the proper location is a particular problem.

These inhibitors consist of very tight emulsions containing high-density materials. The emulsions break slowly to release the inhibitor after the formulation has reached the greatest depth in the system. These formulations cannot be diluted when added to the system.

The effects of mixing the inhibitor, either concentrated or dilute, with the environment of the treated system can be related to inhibitor efficiency and to treatment techniques, and are frequently the cause of undesirable side effects.

8.15.2 Influence of Solubility

Solubility in the environment is necessary if the inhibitor is to reach the metal surface. However, in some cases, the degree of solubility can be related to the inhibitor's effectiveness. Borderline solubility along with polar properties is thought to be an important feature in promoting the effectiveness of a particular molecule as a corrosion inhibitor.

However, as solubility decreases, the amount of inhibitor available is decreased and the ease with which the material reaches the metal surface is diminished. In many cases, it is necessary to disperse the additives so it will be diluted in the process stream sufficiently to dissolve. Thus, along with effectiveness, solubility and dispersibility become important properties in the evaluation of an inhibitor formulation.

Solubility in a two-phase system becomes even more complex. It is necessary to decide into which phase the inhibitor must be dissolved or if it should be distributed between both phases.

8.15.3 Surface-Active Characteristics

The surface-active properties of an inhibitor, in many instances, are inherent in the particular inhibitor molecule, but in some formulations are enhanced by the addition of other chemicals. Surface activity, in addition to influencing inhibitor effectiveness, determines dispersibility and detergency, which in turn affect the emulsion and foaming properties of the system. Detergency, the ability to clean a surface or keep a surface clean, is desirable because of the need for a clean surface onto which the corrosion inhibitor can be adsorbed.

Foam or emulsion formation can seriously affect equipment operation and in a two-phase system can impede separation of the phases when it is necessary to do so. An example of the severe restriction placed on a corrosion inhibitor regarding foam or emulsion formation is that concerning the water tolerance of jet fuel. Water pick-up in the fuel must be limited, so that fuel lines will not freeze and plug during low-temperature operation.

8.15.4 Testing for Solubility, Dispersibility, Emulsion, and Foaming

Solubility, dispersibility and emulsion-forming properties of an inhibitor may be determined in simple bottle tests. Either the actual fluids of interest or some closely simulating them may be used.

The inhibitor is added to bottles at varying concentrations and the bottles are shaken and then observed for total solubility or dispersibility, and the time for the dispersion to separate. If two-phase systems are involved, both should be included in the bottle to find the effects of emulsion formation.

For example, for oil-field use, the bottle tests may include either high or low molecular weight hydrocarbons, aromatic or aliphatic hydrocarbons, brine and mixtures of brine and hydrocarbons.

More elaborate equipment is required to determine certain other properties. The ASTM D-2550 test describes a method to determine water tolerance in jet fuels in which the fuel is emulsified, filtered, separated, and the remaining entrained water is measured as turbidity by a photocell. A less-stringent test for water pick-up is described in ASTM D-2550, where steam is sparged into the hydrocarbon phase and time of cloudiness is measured. Detergency is difficult to evaluate in equipment other than that being treated. In the petroleum industry, detergency of fuels is evaluated in small-scale engines.

Foaming occurs usually where gas evolution or pressure changes occur. The ASTM D-1881 test describes a method for evaluating foaming characteristics in an automotive anti-freeze mixture in which a gas is bubbled at a fixed rate through the fluid of interest and the height of the generated foam is measured. A similar test can be used for any single fluid or mixed phase system.

8.15.5 Formation of Sludges or Precipitates

The use of corrosion inhibitors is often accompanied by treatment with other additives such as scale inhibitors, dispersants, or bactericides. These additives may react with the inhibitor to produce sludges or precipitates that have no protective properties and that may consume the inhibitor, thereby reducing its concentration in the solution.

Two kinds of tests should be carried out to determine the effects of mixing if the chemical structure of each additive is not already known. A bottle test should be carried out in which relatively concentrated solutions of the two additives are mixed and observed for gross reactions, such as the formation of a precipitate.

The second test is one in which each of the additives was originally evaluated. In this test, the additives are mixed at the low concentrations used in treatment and the test results of the mixture are compared with the results using the additive alone. If a significant loss of effectiveness is observed with the mixture, the materials should be considered incompatible.

8.15.6 Ecological Effects

If the treated system is to be ingested by human beings or animals, the additives must have no toxicity. When disposal is to the sewer or to natural water streams, the effect on the environment must be minimal. It is also the responsibility of both the supplier and the user to be aware of government regulations regarding the use of specific chemicals in applications where potential pollution exists.

8.15.7 Effects of Temperature

The use of a corrosion inhibitor at elevated temperatures sometimes requires more tests than the evaluation of inhibitor efficiency alone. Solubility may be affected in an unexpected way as the temperature increases. For example, some organic inhibitors have a lower solubility in brine at elevated temperatures than at ambient temperatures.

In a static system requiring relatively high concentrations of inhibitor, it is essential that the solubility of inhibitor be unaffected by temperatures to which the solution is exposed. Bottle tests can easily evaluate these properties.

Drying and the properties of the resulting film can be important in hot gaseous systems where the carrier solvent will be evaporated. The film should flow at the temperature of the system, should not dry to form flakes that could be abrasive and should be readily soluble in some easily available solvent.

Simple tests can be devised to evaluate these properties, e.g. by applying the neat inhibitor to a hot metal plate and observing the degree of evaporation, the degree of fluidity, and the changes of the film with exposure time.

High-density (weighted) inhibitors are designed to reach the bottom of oil wells by being heavier than oil or brine phases in the well. Contact with brine at the elevated temperature at the bottom of the well causes the emulsion carrying the inhibitor to break and release it into the system. A bottle test has been devised in which the inhibitor is dropped through the hot brine and the time for complete breakdown of the emulsion observed.

8.16 Monitoring of Corrosion Inhibitors

Assessment of the performance of corrosion inhibitors applied either by batch or continuous techniques requires a field monitoring program. A well-designed monitoring program should be supported by normal field records and annual (turnaround) inspections. Field monitoring methods for producing wells include caliper surveys, visual inspection of pull rods and tubing strings and other techniques designed to indicate the condition of the production tubing. Flow lines and junctions may be inspected on an annual basis by techniques such as X-ray ultrasonic testing, Lin-a-log and other surveys.

8.16.1 Water Samples

Samples are collected at wellheads, inlet separators, or intermediate points in the system. Waters are normally analyzed for manganese levels and total iron. Most produced water associated with oil and gas production has extremely low natural manganese levels. Thus, a finding of significant manganese

levels in the water sample is usually indicative of corrosion because any manganese has originated from the steel in the system.

Comparison of manganese levels between wellheads and inlet separators, making allowances for the contribution of each water source to the fluid reaching the separator, can give a measure of the protection achieved along the flow lines. Similar comparisons of iron levels at well heads and inlet separators can be made.

Where a down-hole protection program is in use for producing oil or gas wells, monitoring of the iron and manganese levels in well-head or field-separator samples is an extremely valuable tool for indicating when renewal of inhibitor in a batch program is required.

It should be noted that many produced waters have a significant level of iron originating from the formation. Since the normal manganese content of steel used in oil and gas production is approximately 1%, an iron to manganese ratio that is significantly in excess of 100:1, particularly in well-head samples, is a strong indication of iron originating from the formation. Iron to manganese levels may fall significantly below 100:1 in the case of sour gas fields as the hydrogen sulfide present converts the iron to insoluble iron sulfide that may not be carried forward to the inlet facilities.

Data from laboratory analysis is compared with prior values from the same location. These comparisons alter the user to trends and changes in the system monitored.

8.16.2 Corrosion Coupons

Installation of corrosion coupons changed quarterly, semi-annually or annually in well heads and at suitable points in a gathering system provides very valuable information that good protection is being provided by the corrosion inhibitor used in the system.

Some manufacturers can supply coupons, bull plugs, coupon holders, assist with the installation and coupon changes, and carry out analyses reporting weight changes, pitting rates, and qualitative identification of deposits on coupons installed in the system.

Inhibitor manufacturers fully support all monitoring programs involving coupons with reports giving, not only basic data on the coupons, but full discussions of the results obtained with comparisons for the previous exposure period. This additional information has proven very valuable to many customers in giving indications of changes occurring in a system.

8.16.3 Inhibitor Residuals

Quantitative data, when appropriate, on inhibitor residuals measured in fluid samples collected at suitable points in the field, such as dehydrators, intermediate sample points, and inlet separators should be provided. Knowledge of the residual inhibitor levels, as well as the iron and manganese levels allows the most economic rates to be established for full protection of a particular system.

8.16.4 Electric Resistance Probes and Corrosion Monitoring Probes

Results obtained on field probes can be correlated with chemical analysis data, residual inhibitor data, and corrosion coupon monitoring data.

Successful corrosion control programs depend both on proper application techniques of the protective chemicals and good monitoring. Consistent record keeping by both the supplier and the customer is an essential part of a successful monitoring program.

8.17 Corrosion Behavior of High-Alloy Tubular Materials in Inhibited Acidizing Conditions

The use of corrosion-resistant alloys to fight bottom-hole corrosion due to the presence of H_2S and CO_2 has led to the need for testing such alloys in all expected conditions, typically during acidizing stimulation jobs, which determine very severe corrosion in terms of either general or localized attacks.

While the behavior of carbon and low-alloy steels in inhibited stimulation conditions are well known, few data are available on the corrosion behavior of corrosion-resistant alloys, primarily at high temperatures.

This section deals with the corrosion behavior of duplex stainless steel, some high austenitic stainless steels, and a nickel-based alloy in 28% HCl acidizing solutions, either in inhibited or uninhibited conditions, at 130 °C. Weight loss, crevice corrosion, and stress corrosion cracking tests were carried out for 6 and 24 hours, with amine-based commercial corrosion inhibitors, originally formulated for carbon steel.

8.17.1 Experimental Procedure

The depletion of easy oil and gas fields has led, in recent years, to the exploitation of both new deep reservoirs and already discovered fields that very often produce H_2S and CO_2 at high temperature and pressure, showing, consequently, very severe corrosive conditions. Traditional completion type, i.e. carbon or low-alloy steels, associated with corrosion inhibitors, does not represent a reliable solution from the corrosion point of view.

These alloys should resist corrosion, not only in bottom-hole conditions, but also in all expected conditions, typically during acidizing stimulative operations where highly concentrated mineral acids are used, such as HCl or HCl/HF mixtures.

Currently available corrosion inhibitors were formulated for carbon and low-alloy steels and their performance with standard materials is sufficiently known. Recently some data on the corrosion behavior of corrosion-resistant alloys during acidizing jobs and using standard corrosion inhibitors, became available. However, only few data have been published, restricted to low or medium temperatures, and medium acid concentration.

8.17.1.1 Materials

One laboratory investigation has studied four high austenitic stainless steels and a duplex stainless steel. The low-alloy steel was tested since the corrosion inhibitors used were formulated for carbon and low-alloy steels. Chemical compositions (% by weight) and relevant mechanical properties in as-received conditions are respectively reported in Tables 8.6 and 8.7.

8.17.1.2 Specimens

Potentiodynamic test specimens were disks of 16 mm in diameter, prepared by machining, water grinding, and final polishing with diamond pastes up to 1 μm. All specimens, before and after testing, were degreased by ultrasonic dipping in trichloroethylene first, followed by acetone and distilled water. Weight loss specimens were coupons of about 30 cm^2 in area. Machined surfaces were water-ground with abrasive papers up to 220 mesh.

Crevice corrosion specimens were tailored as Anderson's assembly. For specimens obtained from tubulars, a milling operation was carried out. Surface preparation involved machining, followed by wet grinding up to 600 mesh. Crevice sites were 16 (only one side) for specimens obtained from

Table 8.6 *Chemical compositions (% by weight) of the materials examined*

Alloy	Element										
	C	Cr	Ni	Mo	Mn	Si	Cu	S	P	N	Others
Duplex S.S	0.04	23.3	6	3	1.51	0.33	0.07	0.004	0.013	0.166	Al, 0.022
High austenitic S.S.1	0.017	21.6	36.3	4.5	0.53	0.45	0.5	0.001	0.02	–	Ti, 0.27; W, 0.48
High austenitic S.S.2	0.015	25	38.1	4	0.62	0.18	1	0.001	0.21	0.029	–
High austenitic S.S.3	0.018	27.1	31.3	3.5	1.84	0.82	0.75	0.002	0.015	–	–
High austenitic S.S.4	0.02	26.3	31.9	4	1.6	0.03	1	0.003	0.019	–	–
IN718	0.046	19	52.9	3	0.07	0.14	0.04	0.002	0.007	–	Al, 0.06; Ti, 1.02; Nb + Ta, 5.4
Low-alloy steel	0.24	1.03	0.15	0.16	1.28	0.29	0.1	0.007	0.012	–	Al 0.049; Ti, 0.045; Sn, 0.011

Table 8.7 *Mechanical properties of the materials examined*

Alloy	Yield strength TYS (MPa)	Elongation %	Hardness HRC
Duplex S.S	980	9	29
High austenitic S.S.1	875	15	29
High austenitic S.S.2	800	14	26
High austenitic S.S.3	800	20.8	27
High austenitic S.S.4	770	13	28
IN718 (Thermal treatment: 1 h at 955 °C; A.C. + 8 h 720 °C; F.C. at 55 °C/h to 620 °C; held 8 h; A.C.)	1320	15	43
Low-alloy steel	780	18	27.8

tubulars, and 32 (two sides) for other materials. SCC specimens were C-ring in accordance with ASTM G3079, loaded at 100% yield strength. As far as high austenitic stainless steel 3 is concerned, U-bend specimens were also used, in accordance with ASTM G38-73. Bolts and nuts were made of Hastelloy C-276.

8.17.1.3 Test Solution

Tests were carried out in 28% HCl solution, in both inhibited and uninhibited conditions. Two commercially available acid inhibitors for low-alloy steels were used, whose basic compositions were as follows:

- *Inhibitor A*: Proprietary blend of aliphatic and cycloaliphatic amines, acetylenic alcohols, and surfactants. Concentrations used were both 1% and 2% by volume. Intensifier, when used, was added at the same concentrations.
- *Inhibitor B*: Proprietary blend of acetylenic alcohols, heterocyclic amines, surfactants, and inorganic copper salt. Concentration used was 1% by volume.

8.17.1.4 Test Procedures

Potentiodynamic tests for anodic polarizarion curves were carried out at 80 ± 1°C at a scanning rate of 1200 mV/h, starting from −250 mV versus rest potential. The inhibitor concentrations used were 1% for both inhibitors. The experimental apparatus was as reported in ASTM G5-82 standard practice.

Before starting the test, samples were left in contact with the acid solution for 15 minutes, in order to attain stable corrosion potential values. All potentials were measured against a saturated calomel electrode, maintained at room temperature. The interliquid junction was minimized by using an agar–agar bridge saturated with KCl. The thermogalvanic effect was not taken into consideration.

8.17.1.5 Autoclave Tests

Weight loss, crevice corrosion, and SCC tests were carried out under the following conditions:

- Temperature 130 ± 1.5°C
- Exposure time, both 6 and 24 hours.

The autoclaves, internally clad with tantalum, had a capacity of 1.5 L. The volume of test solution was 1.3 L, leading to a volume/surface sample ratio ranging from 5.9 to 7.2 mL/cm^2. Taking into consideration the autoclave surface as well, the ratio became 1.7 to 1.8 mL/cm^2, which is similar to the volume/ surface ratio for 73 mm (2 7/8 inch) tubing. Special care was taken to avoid galvanic contact between the samples and the tantalum autoclave surface, by hanging the specimen in suitable glass devices.

Oxygen was not removed from the HCl solution and autoclave gas cap, at test start-up, was air. Some tests were also carried out at 80 °C on the duplex stainless steel in a glass cell and the results are presented in Table 8.8.

8.17.1.6 Potentiodynamic Tests

The aim of the test was primarily the establishment of a mechanism for the corrosion inhibitors. Accordingly, it resulted that, at 80 °C, both inhibitors moved the rest potential of all tested materials toward more noble potential values and showed a strong influence on the cathodic curve, giving rise to a decrease in circulating current of two decades on average.

Table 8.8 *Corrosion inhibitor efficiencies at 80 °C; Z = (iun − iin)/iun*

Alloy	Corrosion current densities (mA/cm^2)			Inhibitor efficiency	
	Uninhibited	Inhibitor A	Inhibitor B	ZA	ZB
Low-alloy steel	46	0.78	0.018	98.3	99.96
Duplex S.S	56.1	0.136	0.03	99.95	99.96
High austenitic S.S.1	0.15	0.036	0.0042	76	97.2
High austenitic S.S.2	0.48	0.033	0.0024	93.1	99.5

Table 8.9 *Corrosion rates (mm/year) in 28% HCl at 130°C*

Alloy	Experimental conditions									
	Not inhibited	Inhibitor A 1%		Inhibitor A 2%		Inhibitor A 1% + Intensifier 1%	Inhibitor A 2% + Intensifier 2%		Inhibitor B 1%	
	(6 h)	6 h	24 h	6 h	24 h	(24 h)	6 h	24 h	6 h	24 h
Duplex S.S.	2900	405	540	1250	1150*	595	2260	570	500	90
High austenitic S.S.1	250	2.8	2	1.2	1.7	1.2	4.8	2	0.4	0.25
High austenitic S.S.2	440	3	2.5	2.5	2	1.6	6.2	2.2	0.5	0.23
High austenitic S.S.3	1470	20	14	3.6	12.2	13	4.8	1.6	0.5	0.42
High austenitic S.S.4	1340	4.4	13	2.5	2.5	23	7.5	3	0.7	0.25
IN 718	180	3.4	8	2	2	50	4.2	2	12	0.25
Low-alloy steel	2500*	545	650*	420	650*	2500*	1090	650*	250	25

*Specimen totally corroded after test

Table 8.10 *Weight losses and corrosion rates for duplex stainless steel at 80°C*

Exposure time (h)	Weight losses (kg/m^2)			Corrosion rates (mm/y)		
	Uninhibited	Inhibitor A 1%	Inhibitor B 1%	Uninhibited	Inhibitor A 1%	Inhibitor B 1%
6	–	0.0097	0.029	–	1.8	5.42
24	13.86	0.068	0.244	531	3.39	11.15

Table 8.11 *Results of the crevice corrosion tests in 28% HCl at 130°C*

Alloy	Experimental conditions						
	Uninhibited	Inhibited (6 hours)			Inhibited (24 hours)		
		Inhibitor B 1%	Inhibitor A 1%	Inhibitor A 1% +Intensifier 1%	Inhibitor B 1%	Inhibitor A 1%	Inhibitor A 1% +
Duplex S.S	Very high dissolution	CC	Very high dissolution	Very high dissolution	–	–	–
High austenitic S.S.1	Protection	Very light CC	Light CC	CC	CC	CC	CC
High austenitic S.S.2	Protection	No CC	Very light CC	Light CC	Light CC	CC	CC
High austenitic S.S.3	Protection	Very light CC	Light CC	CC	CC	CC	CC

CC: Crevice corrosion

Table 8.12 *Results of stress corrosion tests in 28% HCl at 130 °C*

Alloy	Experimental conditions	
	Uninhibited (6 h exposure)	Inhibited (6 and 24 h exposure)
Duplex S.S.	Very highdissolution	No SSC
High austenitic S.S.1	SSC	No SSC
High austenitic S.S.2	SSC	No SSC
High austenitic S.S.3	SSC	No SSC

Inhibitor efficiencies were calculated from potentiodynamic tests by determining the corrosion current densities (Table 8.8). Results confirmed good efficiencies at 80 °C of corrosion inhibitors for all the materials.

8.17.2 Weight Loss

All results are reported in Tables 8.9. and 8.10, where weight losses are reported and compared with the maximum accepted practical value, which is 0.244 kg/m^2 (0.05 lb/ft^2) for each single acidizing operation; calculated corrosion rates are also reported.

8.17.3 Low-Alloy Steel

Although data reported by suppliers on technical information brochures, low alloy steels, exposed to inhibited solutions, exhibited in laboratory test conditions severe corrosion rates, higher than maximum allowed. Most likely this is primarily due to the high temperature and relatively long exposure time. Of the two corrosion inhibitors tested, that designated B showed a better effectiveness in all experimental conditions.

8.17.4 Crevice Corrosion

High austenitic stainless steels, in the presence of corrosion inhibitors, suffer crevice corrosion attacks occurring in all locations. Table 8.11 shows the results of the crevice corrosion tests in 28% HCl at 130 °C. All results of SCC tests are reported in Table 8.12.

8.17.5 Conclusions and Recommendations

Laboratory tests, carried out in 28% HCl solution at 130 °C, showed the following results:

- Commercial corrosion inhibitors, formulated for low-alloy steels, showed good effectiveness when used with high austenitic stainless steels and nickel-based alloys.
- Low-alloy steels, exposed to inhibited solutions under laboratory test conditions, exhibited severe corrosion rates, higher than the maximum allowed.
- The behavior of duplex stainless steel, also in the inhibited solution, was very poor at 130 °C. At this temperature, galvanic coupling was operating, despite the presence of inhibitor; however, at

80 °C the behavior was acceptable. As a consequence, there is a need for better inhibitors for high operating temperatures.

- Crevice corrosion tests revealed susceptibility to corrosion attack in the presence of corrosion inhibitors, while in their absence no preferential attack in crevice sites was observed.
- SCC, in the presence of commercial inhibitors, did not occur for any tested materials; in the absence of corrosion inhibitors, transgranular microcracks were present at the bottom of pits on high austenitic stainless steel.

9

Compatibility in Material Selection

The designer should always consider the structure and equipment as a whole and should avoid regarding individual items in isolation because this is not actually true in practice. It is imperative that all intermaterial influences are properly evaluated before any final decision is taken on a design. Compatible materials will not cause uneconomic breakdown within the utility. This section is concerned with the various types of intermaterial relations met in engineering design.

Badly conceived relations between individual materials of a complex can ruin even the best design. Thus it is imperative that all intermaterial relationships are properly appreciated and evaluated before any final decision in design is taken, whether these are caused by direct contact between dissimilar metals or induced by changes in polarity, transfer of electrolysis through a medium, carrying metallic particles in the stream, the adverse influence of stray currents, or by any other negative effect arising from the near proximity of materials (e.g. chemical, thermal, or radiation) selected to form the required unit.

In complex structures and equipment, process streams, and piping arrangements, different metals, alloys or other materials are frequently used in corrosive or conductive environments within an easy reach of each other; in practical applications contact between dissimilar materials cannot be totally avoided.

It is up to each individual designer to create benign conditions of contact between the various materials and units within the project design, and to take proper precautions to avoid the consequences of less optimal selections enforced by predominantly functional requirements. These precautions will mainly consist of selecting compatible materials, designing effective electric separation, and adjusting environmental media.

Compatible materials are those that, although used together in a particular medium in appropriate relative sizes and compositions, will not cause an uneconomic breakdown within the utility. Materials do not only influence each other by virtue of their inherent or induced difference in electric potentiality (electrochemically), but also by their composite chemistry. These adverse chemical influences may be caused by materials in the ambient state or induced by changes in materials caused by

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variations in environmental conditions. All the above-mentioned possibilities will have a bearing on the designer's appreciation of the problem.

Not all considerations are, however, given to the adverse effects of the proximity of materials. There are several situations where, by judicious choice of dissimilarity between materials, beneficial results can be obtained (e.g. sacrificial cathodic protection, cleaning of metals).

9.1 Requirements for Compatibility

Compatibility in design depends on the following parameters:

- Component metals or other materials
- Differences in emf
- Distance between dissimilar materials
- Degree of exposure to corrosive environment
- Relative sizes of anode to cathode, or of a contaminator to the affected material
- Conductivity of environment versus conductivity of materials
- Resistivity of environment versus resistivity of materials
- Temperature gradients and spread
- Fluid current strata, directions, and velocities
- Contents of cathodic metals or aggressive materials in liquid media or atmospheres
- Criticality of resultant failures
- Sources of DC stray currents and their conductive paths
- Development of corrosive fumes in specific conditions
- Nature of the effect – beneficial or detrimental, etc.

Dissimilar metals in intimate contact or connected by conductive path, such as water, condensation, or electrolyte, should be applied only when the functional design renders this unavoidable. If the use of dissimilar metals is necessary, an attempt to select metals which form "compatible couples or groups" should be made. The "Galvanic Corrosion Indicator" published by the International Nickel Company Ltd. can be useful. Table 9.1 shows examples of other environments with different indicators.

The scales of galvanic potentials are meaningless unless the amount of current flowing between dissimilar metals is known. The designer should obtain accurate information on the material composition of all items. Galvanic corrosion of dissimilar metals can be avoided by preventing the extended presence of humidity (e.g. condensation) at the joints. Bimetallic connections in the proximity of fumes from combustion generators should be avoided.

Connections between stainless steel and steel, or stainless steel and aluminum components in a conductive environment are considered to be bimetallic couples, and selective precautions against galvanic action should be taken.

Faying surfaces of dissimilar metals should be separated completely and effectively (see Figure 9.1).

Where complete dielectric separation cannot be implemented, any possible increase in the electrolyte path should be advantageous. Dielectric separation can be provided in miscellaneous ways:

- Insulating gaskets (synthetic rubber or PTFE and other non-porous materials) for shaped contacts
- Butyl tape (minimum 0.51 mm thick) for linear extended contacts
- Spreadable sealant (two coats to each surface) for multi-form or small-sized contacts, etc.

Table 9.1 *Grouping of compatible materials air space environment*

Type 1	Inert environment	All materials are compatible
Type 2	Humidity controlled heated and/or air-conditioned building	Platinum, gold, graphite and silver are not compatible with low-alloy steel, aluminum, magnesium, copper, and cadmium – other combinations are compatible
Type 3	Interior of unsheltered vehicles, uncontrolled humidity	I. Magnesium II. Beryllium, zinc, clad and non-clad aluminum alloys, cadmium III. Steel (except corrosion-resistant), lead, tin IV. 12% Cr 400 series steels, pH corrosion-resistant steels, 18% Cr 400 series steels, chromium, brass, bronze, copper, beryllium copper, aluminum, bronze alloys, 300 series stainless steels, Monel, Inconel, nickel alloys, titanium alloys V. Silver, graphite, gold, platinum. (Note: Each material is compatible with other members of the same group but not with materials of a different group with the following exceptions: Titanium fasteners installed in aluminum alloys are considered similar. Titanium is similar to group V metals Tin is similar to group II alloys Graphite composites are considered similar to group V metals and the last five members of group IV
Type 4	Exterior of unsheltered vehicles	Titanium alloys, nickel-based and cobalt-based alloys (Inconel), 300 series stainless steels, gold, platinum, and graphite are compatible with each other, but not with other materials

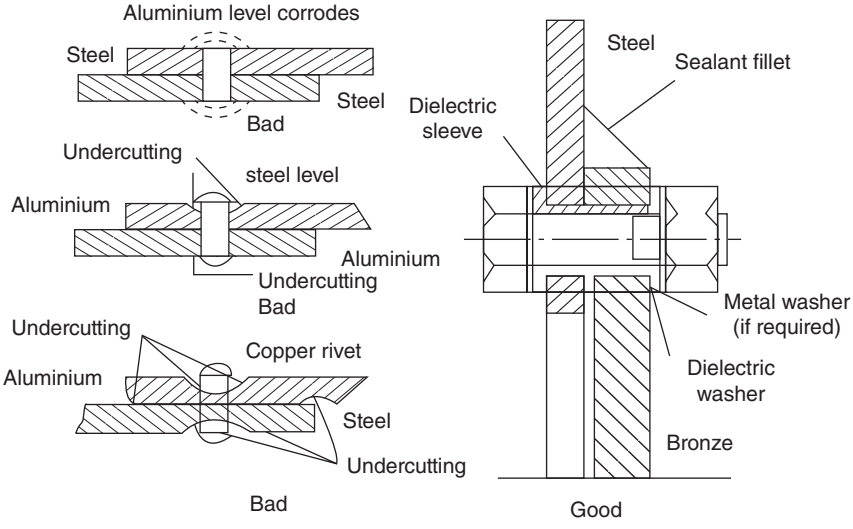


Figure 9.1 *Separation of faying surfaces of dissimilar metals. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

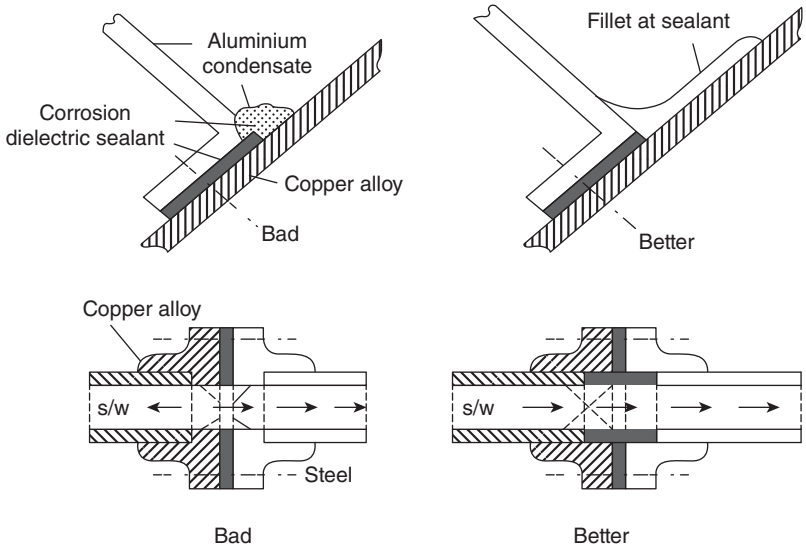


Figure 9.2 *Thickness and coverage of insulation and adjustment of environment. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

Electrolytic reaction between dissimilar metals submerged in conductive liquid media, or where deposited liquid connects metals over dielectric insulation, can by-pass this insulation. The insulation should then be of sufficient thickness and coverage, and an adjustment of the environment may be necessary (by inhibition or by cathodic protection; see Figure 9.2).

Where dielectric separation between dissimilar metals cannot be used, a metal that reduces the potential difference between the two metals can be interposed (see Figure 9.3 a, b, c):

(a) Separate solid metal
(b) Clad metal sandwich
(c) Metal sprayed coating of both metals of the joint (fixed or mobile).

Formation of crevices between dissimilar metals shall be avoided; corrosion of such connections is more severe than either galvanic corrosion or crevice corrosion on their own (see Figure 9.4).

In marine and other conductive atmospheres, the adverse effect of galvanic coupling is apparent within approximately 5 cm (2 inches) around the contact. Dielectric separation within this range should be effective, or appropriate compensation for weight/strength loss should be made.

Every effort shall be made to avoid the unfavourable area effect of a small anode and a large cathode. Corrosion of a relatively small anodic area may be 100–1000 times greater, in comparison with the corrosion of bimetallic components that have the same area submerged in a conductive medium (see Figure 9.5).

Less noble (anodic) components should be made larger or thicker to allow for corrosion. Provision should be made for easy replacement of this type of structural unit or component (see Figure 9.6).

In a conductive environment, no less noble part should be inserted haphazardly into an otherwise unified system. Brazing or welding alloys, when used, should be more noble (cathodic) than at least one of the joined metals in galvanic connection, and always be compatible with both.

Below are some recommendations on compatibility that should be considered at the design stage.

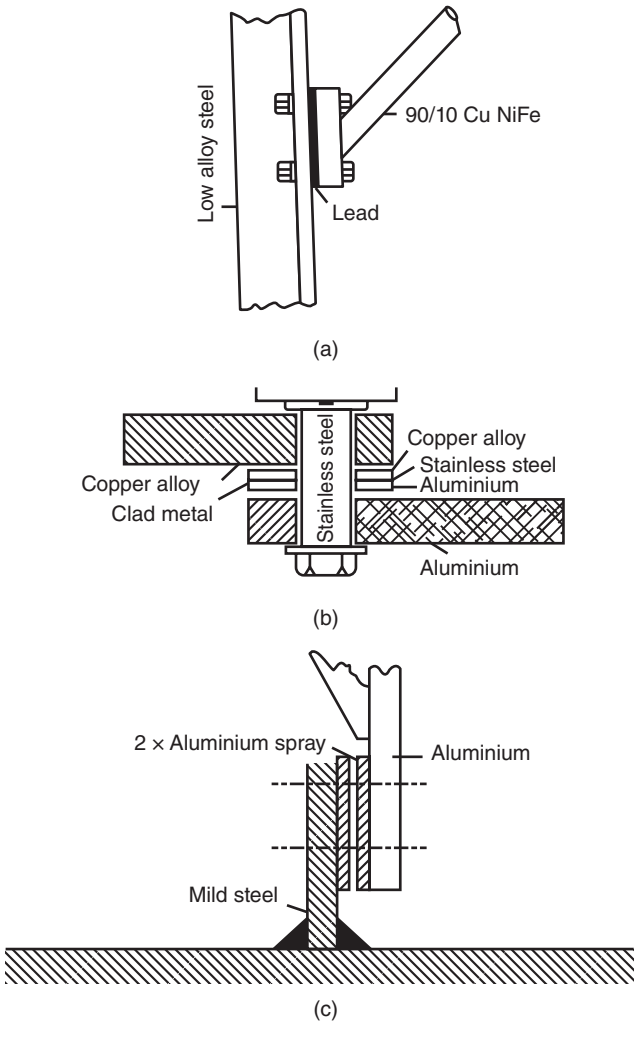


Figure 9.3 *(a) Separate solid metal; (b) clad metal sandwich; (c) metal sprayed coating of both metals of the joint (fixed or mobile). (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

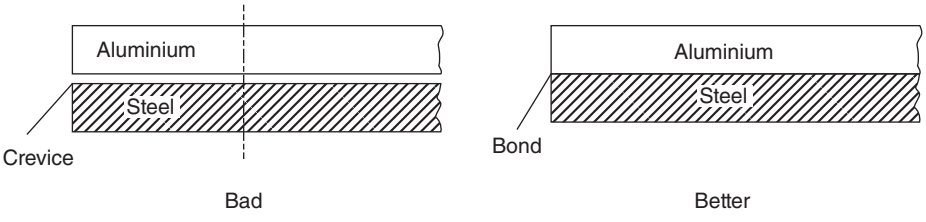


Figure 9.4 *Explosion-bonded clad metals. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

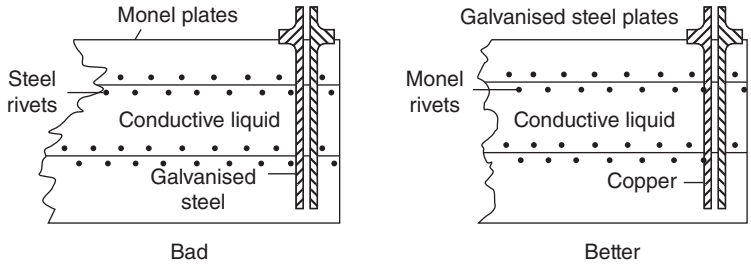


Figure 9.5 *An example of how to avoid the unfavourable area effect of a small anode and a large cathode. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

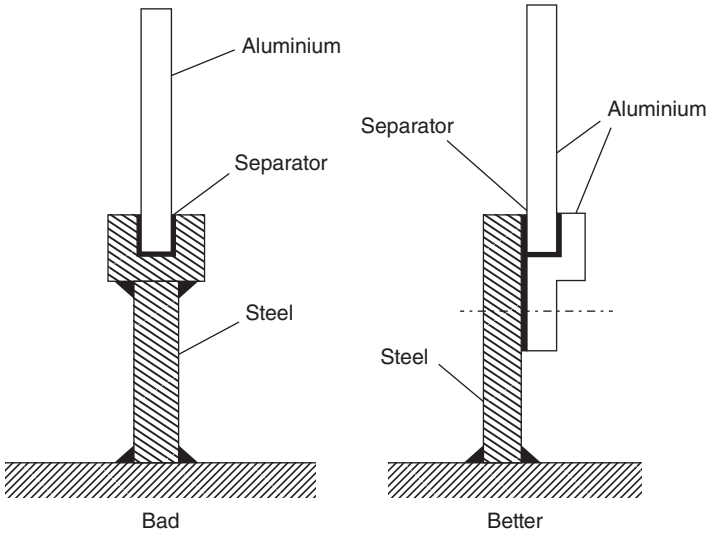


Figure 9.6 *Replacement of less noble (anodic) components. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

9.2 Structures and Equipment

An assembly of dissimilar metals in a design should be preselected on a well-balanced utilitarian basis with compatible affinity. Figure 9.7 shows how the excess insulation compound squeezed out of the joint, augmented with sealing compound if necessary, should be formed into sealing fillets. Welds and other points of high corrosion incidence in proximity should be included within the fillets.

Clad metals may be subject to galvanic corrosion along exposed edges, if the metals are far apart, according to a galvanic corrosion indicator (e.g. copper/aluminum clad to aluminum; see Figure 9.8).

The correct system and sequence of welding attachment of bimetallic pads should be specified to avoid distortion and input stresses (see Figure 9.9).

Figure 9.10 shows an example of a non-adjustable steel filling secured to an aluminum structure.

Canvas fabric impregnated with copper salts should not be attached to steel or aluminum structures, or used as a rain cover for steel or aluminum equipment.

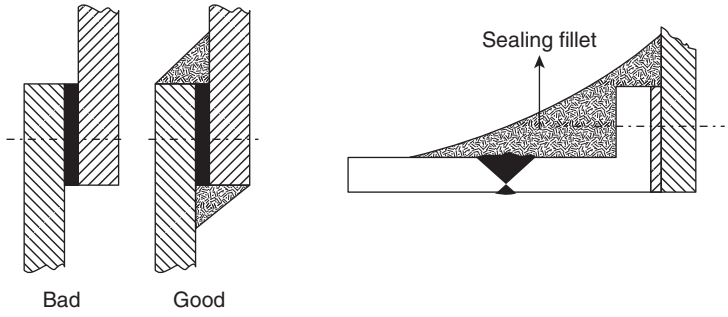


Figure 9.7 *The excess insulation compound squeezed out of the joint should be used to form a sealing fillet. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

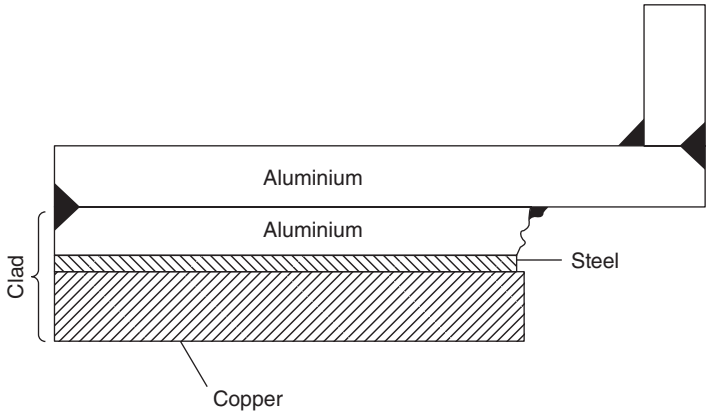


Figure 9.8 *Copper/aluminum clad to aluminum. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

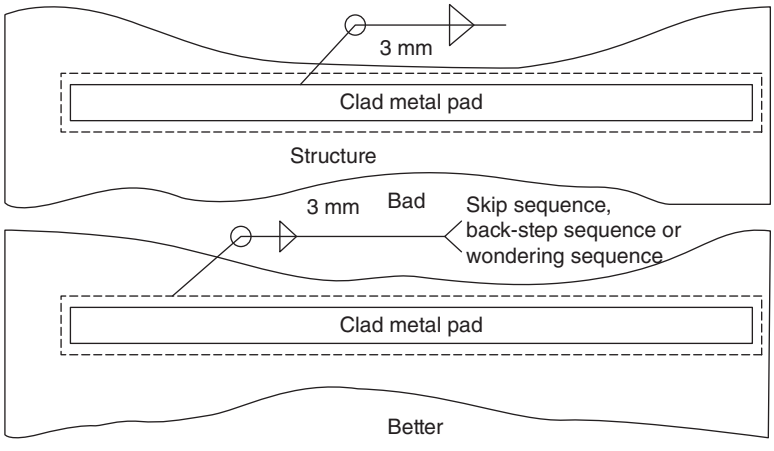


Figure 9.9 *Correct system and sequence of welding attachment of bimetallic pads. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

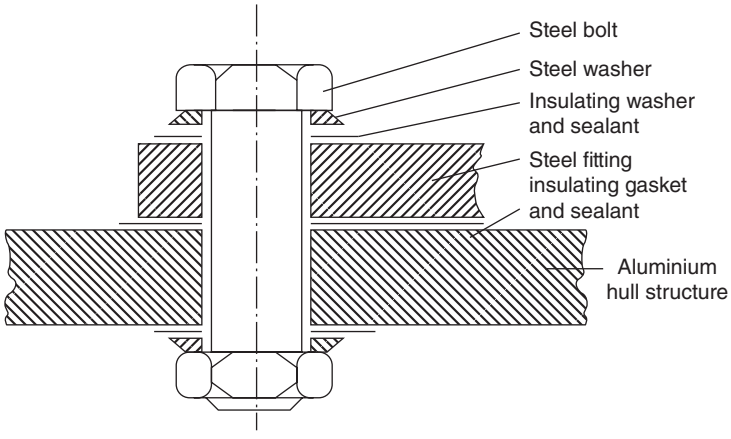


Figure 9.10 *A non-adjustable steel filling secured to an aluminum structure. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

9.3 Piping Systems

Figure 9.11 shows secure, complete, and effective separation between sections of piping composed of dissimilar metals (see Figure 9.11).

Galvanic corrosion of dissimilar metal pipe connections exposed to low conductivity, recirculated, distilled, or demineralized water (when sulfate is present) can be reduced by interposing lead inserts as separators between the faying surfaces of the two metals.

To avoid the adverse effects of graphite and carbon (e.g. solid graphite seals, graphite gaskets or packing) in pipe systems containing conductive media upstream of heat exchangers and other critical equipment (see Figure 9.12), use inert seals and packing.

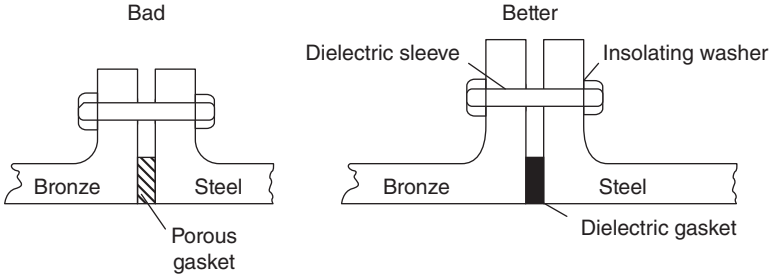


Figure 9.11 *Secure, complete, and effective separation between sections of piping composed of dissimilar metals. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

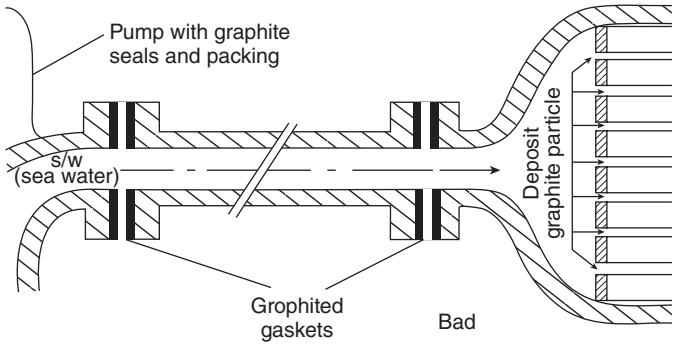


Figure 9.12 *An example of graphite and carbon in pipe systems. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

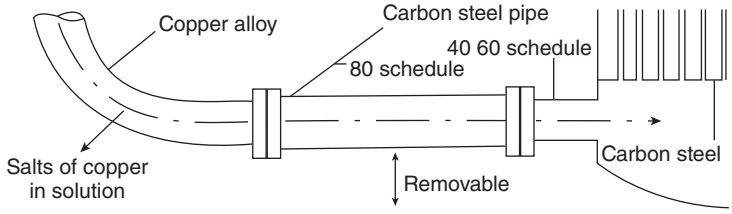


Figure 9.13 *A typical fitting of copper alloy pipes upstream of carbon steel equipment. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

Copper salts emanating from copper-based pipes and carried in solution are dangerous to carbon steel components and tanks downstream. If possible, avoid fitting copper alloy pipes upstream of carbon steel equipment; if such fitting is necessary, interpose sacrificial pieces of mild steel pipe between such connections – these should be in visible range and easily replaceable, and the thickness of their walls in keeping with the planned maintenance program frequency (see Figure 9.13).

Pickling and passivation of Monel and stainless steel pressure vessels will prevent deep pitting, by removing residual ferrous particles. Where pipelines penetrate partitions or bulkheads made of dissimilar metals, precautions should be taken against galvanic corrosion.

In heat exchangers using copper coils the effect of copper going into solution and affecting the galvanized steel shell can be avoided by nickel-plating the coils; these can then be separated by insulation from direct contact with the tank (see Figure 9.14).

Accidental contact of buried pipelines with structures of dissimilar metals and other pipelines should be avoided (see Figure 9.15).

Tool scars on steel pipes that are submerged or buried should be removed – scars are anodic and corrode much faster than the rest of the pipe.

Tinning of copper pipes or components can reduce the galvanic effect between dissimilar metals of an assembly (see Figure 9.16).

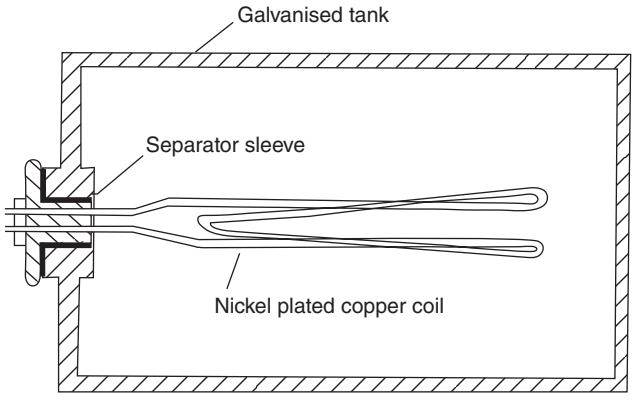


Figure 9.14 *Nickel-plating a copper coil. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

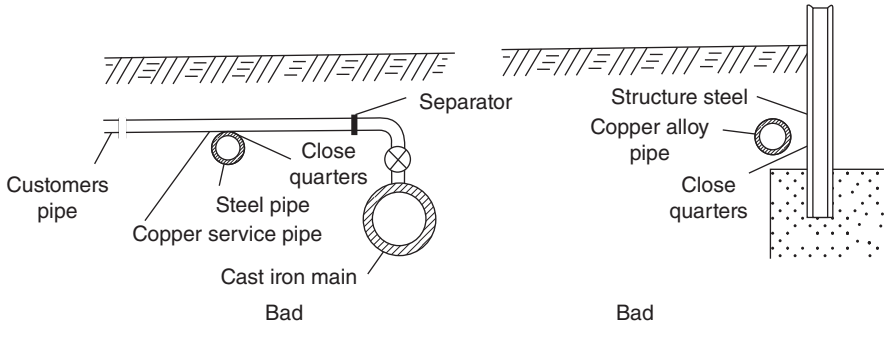


Figure 9.15 *Avoid accidental contact of buried pipelines with structures of dissimilar metals and other pipelines. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

9.4 Fasteners

Fasteners in dissimilar metal connections that are not compatible with either one or both of the metals in the joint, should be effectively separated from the non-compatible metal or metals by dielectric sleeves and washers (see Figure 9.17).

If dielectric separation of fasteners in non-compatible joints cannot be implemented, the fasteners should be coated with zinc chromate primer and their exposed ends encapsulated (see Figure 9.18).

For dissimilar metal connections (aluminum to steel) in a marine environment, stainless steel fasteners installed with heads on the weather side are preferred. Fasteners should be dipped in zinc chromate primer or sealing compound. If stainless steel cannot be used, the exposed ends of fasteners should be encapsulated.

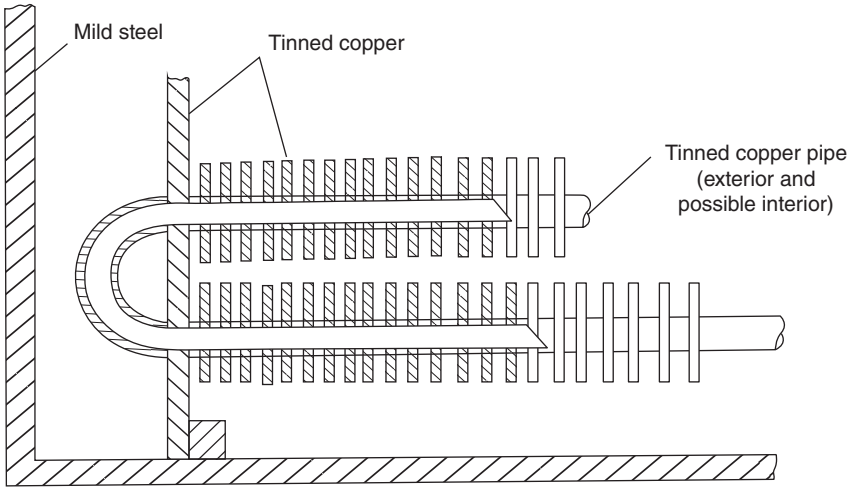


Figure 9.16 *Tinning of copper pipes and components. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

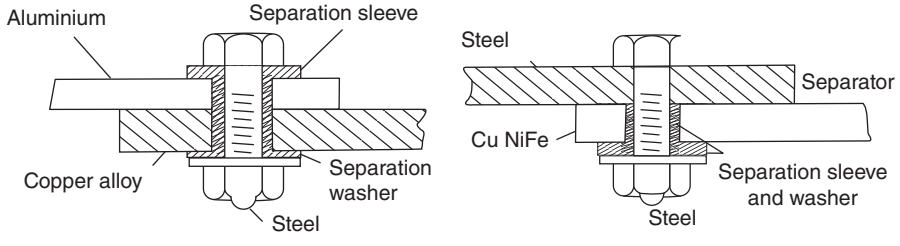


Figure 9.17 *Fasteners in dissimilar metal connections that are not compatible separated from the non–compatible metal or metals by dielectric sleeves and washers. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

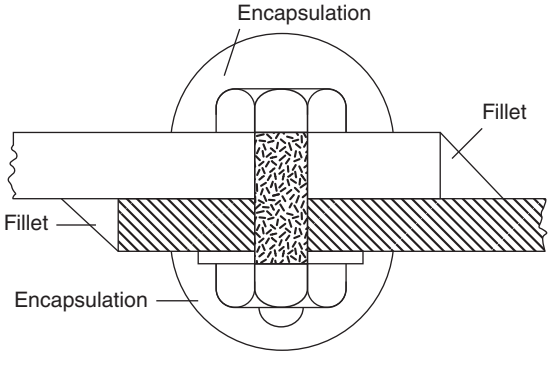


Figure 9.18 *Coated fastener with zinc chromate primer and the exposed ends encapsulated. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

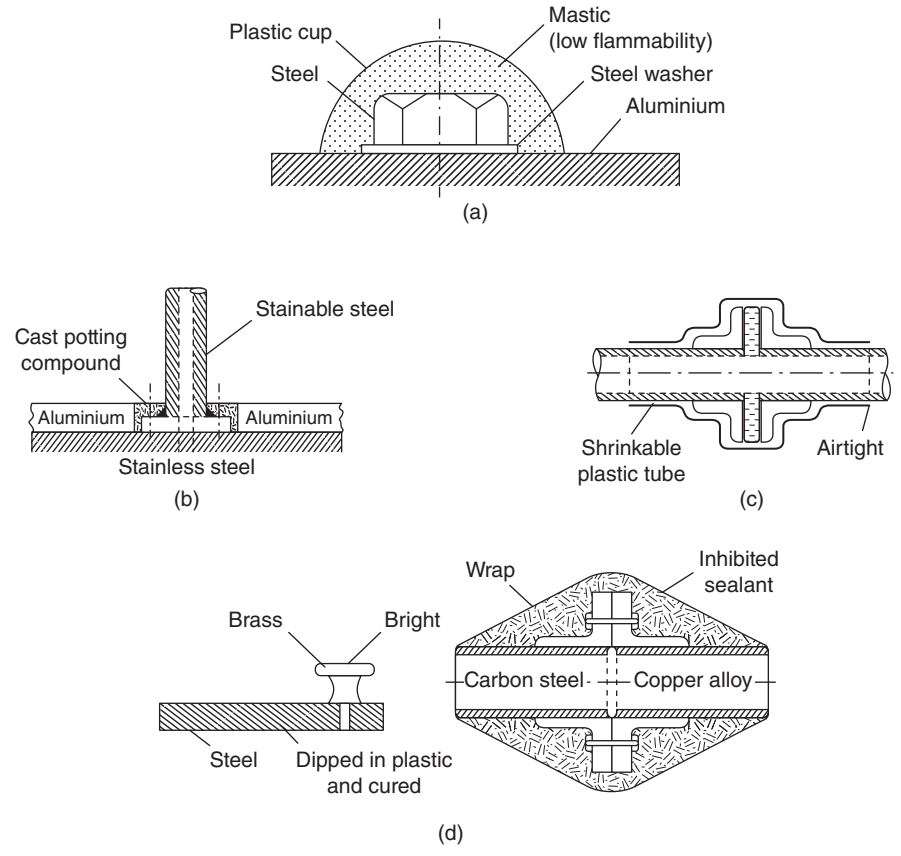


Figure 9.19 *Exclusion of the environment from bimetallic joints using sealing, encapsulating, or enveloping with shrinkable plastic. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

9.5 Encapsulation, Sealing, and Enveloping

If exclusion of the environment from bimetallic joint by geometrical arrangement is not possible, sealing, encapsulating, or enveloping with shrinkable plastic should be used (see Figure 9.19):

(a) Plastic caps containing mastic
(b) Potting compounds (i.e. solventless epoxide) cast
(c) Total or partial envelopment with shrinkable plastics (air and watertight) or plastic films
(d) Application of moisture-proof coating or organic sealant.

9.6 Electrical and Electronic Equipment

The use of dissimilar metal connections should be restricted to compatible metals. If dissimilar metals in contact must be used, the cathodic part should be smaller than the anodic part, whenever

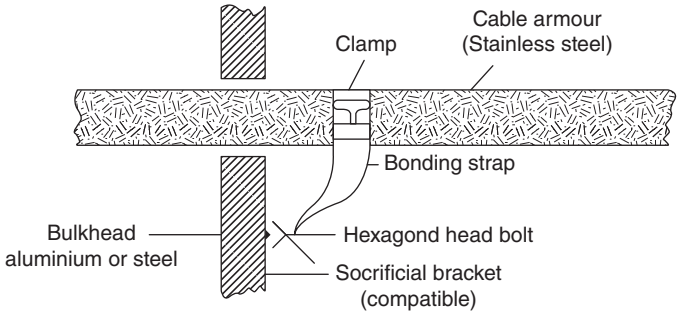


Figure 9.20 *Galvanic corrosion for cable armor grounding at bulkhead penetrations. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

practicable. Galvanic couple connections should be avoided for critical assemblies (safety or operation). Tin-or nickel-plated parts may be mounted directly on an aluminum chassis; for exterior applications, nickel-plated parts should not be in contact with aluminum without a dielectric separator.

Where electrical cables penetrate a dissimilar metal partition or bulkhead, precautions against galvanic corrosion should be taken. Cadmium- or zinc-plated parts or zinc-based alloy parts should not be used within or in the proximity of electrical equipment subject to phenolic vapors emanating from insulating materials, varnishes, or encapsulating compounds.

Connections between magnesium and a dissimilar metal should be separated by an aluminum alloy 5052 gasket installed between the two metals, and the joint should be sealed.

Adequate precautions should be taken against galvanic corrosion for cable armor grounding at bulkhead penetrations (see Figure 9.20).

9.6.1 Grounding and Bonding of Electrical Equipment

Electrical circuits and equipment, especially dc generators, should be designed so that exposed parts or other surface-conductive materials are at ground potential at all times. When the grounding cable and the structure are compatible, grounding, when practicable, should be arranged by means of a bus-strap or shear-splice joint adequately insulated on the exterior.

Copper alloy grounding conductors should not be directly attached to steel or aluminum strength structures or pipe systems, but to a suitable sacrificial bracket. The material of the bracket should be compatible with the structure and a good conductor of electricity. Bonds made by conductive gaskets or adhesives and involving dissimilar metal contact should be sealed with an organic sealant (see Figure 9.21).

When aluminum is to be electrically bonded, preference should be given to the use of clad alloys. Surfaces to be bonded should be masked prior to anodizing or the insulating anodic film removed after anodizing. When an electrical bond is to be made between dissimilar metals, the surface of one or both should be coated with a metal compatible with both metals in the connection. An example of sacrificial bracket is shown in Figure 9.22.

Provide for complete bonding of unified piping systems containing conductive liquids between individual components, by using conductive fasteners, conductive gaskets, or bond straps (see Figure 9.23).

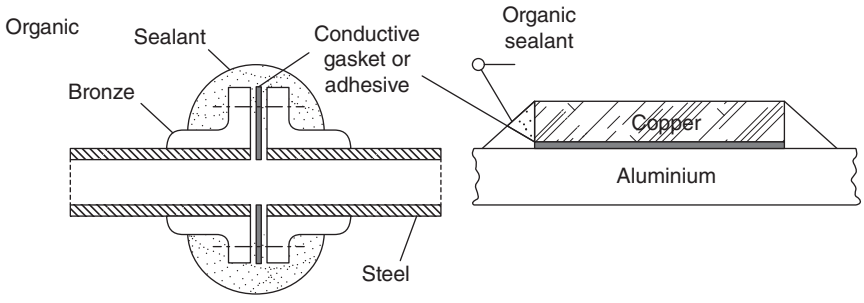


Figure 9.21 *Bonds made by conductive gaskets or adhesives and involving dissimilar metal contact sealed with an organic sealant. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

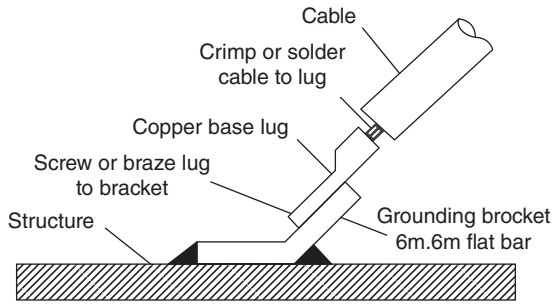


Figure 9.22 *Example of sacrificial bracket. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

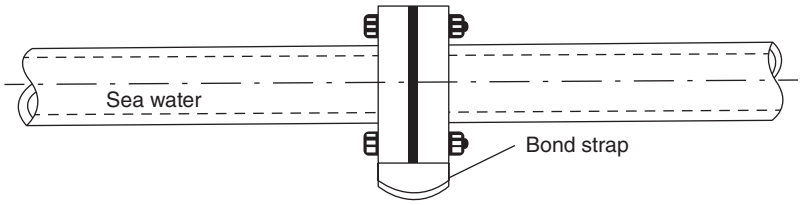


Figure 9.23 *Complete bonding of unified piping systems containing conductive liquids between individual components by bond straps. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

9.7 Coatings, Films, and Treatments

The component materials of the joint should be cleaned, pretreated, and primed prior to assembly in normal conditions. Where design or functional requirements preclude the use of dielectric separation, metallizing (sherardizing, galvanizing, electroplating, cladding, or metal spraying) with anodic metal

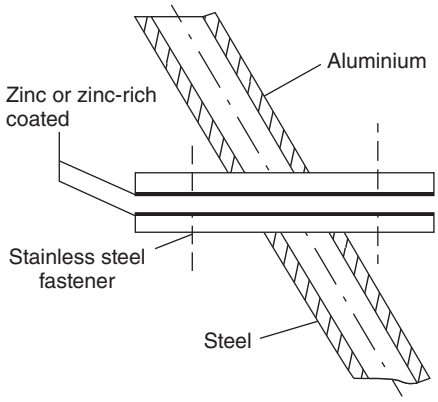


Figure 9.24 *Zinc-rich paint reduces or delays the galvanic reaction between the base metals. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

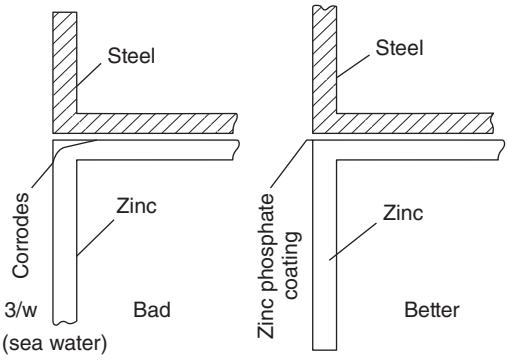


Figure 9.25 *The effect of conversion coatings (chromates, phosphates) applied to dissimilar metal couples. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

(to one or both members of the connection) of all or at least some of the faying surfaces (components, fasteners, etc.), or coating with sufficient dry thickness (0.08–0.38 mm) of zinc-rich paint, can help to reduce or delay the galvanic reaction between the base metals (see Figure 9.24).

When using metallic coating over the whole bimetallic assembly, the coating metal should be less noble than either of the component metals – or at least the cathodic one. Anodic films on aluminum-based alloys should be considered a part of the dielectric separation.

The effect of conversion coatings (chromates, phosphates) applied to dissimilar metal couples can vary (see Figure 9.25):

- Chromate and phosphate-treated zinc- and cadmium-coated metals are not dielectrically separated when in contact
- **C**hromate and phosphate-treated metals in a dissimilar metal couple may sometimes obtain a reduction of galvanic corrosion caused by electric current transfer in a conductive medium.

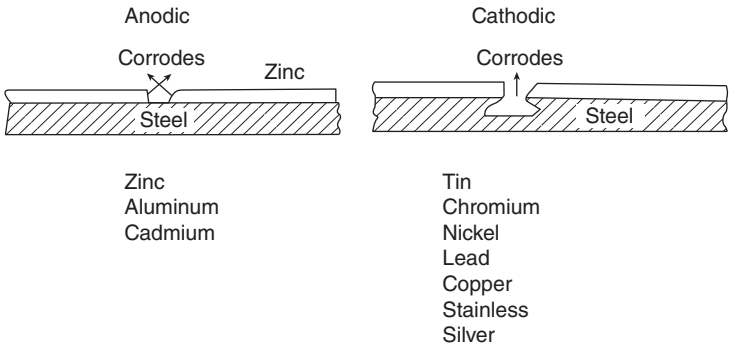


Figure 9.26 *The individual galvanic effect of metallic coatings. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

The individual galvanic effect of metallic coatings should be evaluated before their application in a design for corrosion prevention (see Figure 9.26).

Zinc, as a coating of reinforcing rods and other steel embedded in concrete, helps to prevent or delay formation of rust on such reinforcement in a marine environment.

For mobile joints, various combinations of metallizing and plastic coating can be used (e.g. nylon) instead of dielectric separation between dissimilar metals.

9.8 Chemical Compatibility

The use of materials for design of connections that are mutually incompatible by reason of their chemical contents under particular environmental conditions, e.g. vulcanized rubber, which contains sulphur, affecting metal in contact, etc. should be avoided.

Materials that, under ambient conditions or when under fire or in high-temperature conditions, outgas or liberate corrosive fumes in the proximity of vulnerable materials that can be adversely affected by such fumes and their functional stability impaired should not be used:

- Partially cured or under-cured organic materials
- Insulating materials emitting phenolic vapors, varnishes, or encapsulating compounds within totally unventilated spaces of electronic equipment containing cadmium- or zinc-plated or zinc-based alloy parts
- Vinyl paints emitting hydrochloric acid vapors at temperatures over 66 °C (150 °F).

Where phenolic insulating materials, varnishes or encapsulating compounds must be used in electrical or electronic equipment, and these are subject to elevated temperatures in enclosed spaces, cadmium- or zinc-plated components should be avoided.

Contact between strength materials and any auxiliary materials, compounds, wood or textiles, which by leaching of any contained chemical corrosive on to the surfaces of the strength materials, can materially reduce the functional strength of these critical structures or components are also best avoided:

- Acid contents in wood
- Copper salt impregnation of wood or canvas
- Zinc chloride treatment of timber (zinc or zinc coatings); preservatives based on chromates or arsenates are preferred.

The use of galvanized fasteners in contact with stainless steel structures or components subject to temperatures in excess of the melting temperature of the zinc, etc. is not recommended.

Avoid, where possible, burying steel pipes in strongly acidic soils (lack of polarization); lead or aluminum should not be used for buried structures, equipment, and pipes in highly alkaline soils. Provide, if necessary, for a change of surrounding media (backfill, sand pads); use insulating coatings, cathodic protection and either separately or in combination.

9.9 Environment

Galvanic corrosion of dissimilar metals can be eliminated, delayed, or at least reduced by induction of environmental changes at bimetallic connections:

- Change of temperature
- Reduction or increase of aeration to suit the metals
- Reduction or increase of movement of fluids to suit the metals
- Adjustment of chemistry.

The concentration of the inhibitor should be increased for reduction of galvanic corrosion in comparison with that used for reduction of corrosion of a single metal. A corrosion inhibitor (zinc chromate, zinc chromate paste, etc.) for galvanic connections should be specified when possible.

9.10 Stray Currents

Avoid passage of electric current between metal and its environment, e.g. buried or submerged pipelines, tank bottoms and structures, electric traction, welding plants, power undertakings, and cathodic protection schemes.

Insulating couplings should be used to separate metallic structures for control of stray current corrosion (see Figure 9.27).

The current jump depends on the magnitude of the potential difference, the electrical conductivity of the liquid in the pipe, soil, or surrounding medium, the geometric configuration of the pipe or structure and insulator, the temperature, and any surface films.

A major increase in the length of the separator (e.g. a short length of non-metallic pipe) has no great effect on control of the external current jump (e.g. in soil or other conductive media).

Surface films on the metallic structures involved influence the effect of the separator length (see Figure 9.28).

Local sources of stray currents should be determined and evaluated for their effect on the designed utility (underground and submerged).

The leakage current can be reduced by increasing the resistance between the source and earth, by rail bonding, and rialto-negative ties, by increasing the conductivity of the conductor (rail, lead), by proper scheduling of substation operation, or by welding across each rail section.

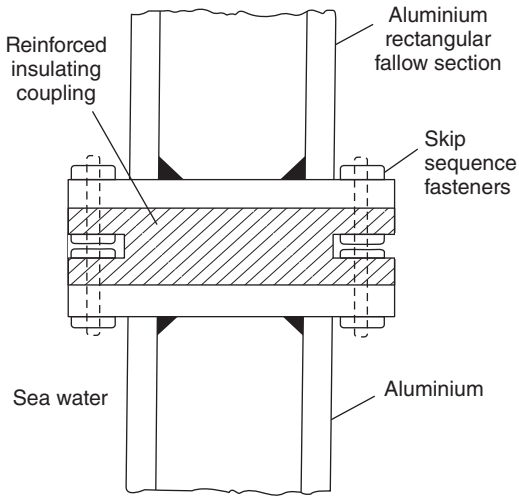


Figure 9.27 *Insulating couplings to separate metallic structures for control of stray current corrosion. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

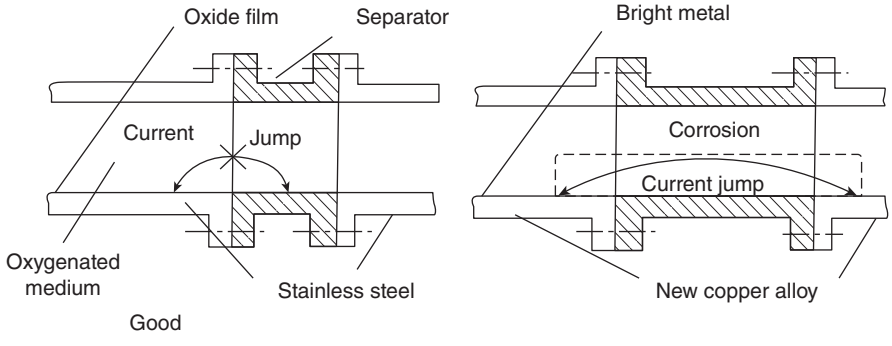


Figure 9.28 *Surface films on metallic structures influence the effect of the separator length. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

The pick-up or discharge of leakage current on the critical structure is reduced by increasing the earth contact resistance, by providing isolation from the earth, by using an insulating coating (organic liquid or tapes), by changing over to non-metallic materials, by placing the structure in conduits, and by flushing the ducts with water in highly salted areas.

Where possible the continuity of the leakage current path back to the substation should be interrupted by introduction of insulating couplings in the critical structure. Where continuity of plant, for protection or interference reasons is necessary, the insulating couplings can be bridged with resistors or capacitors. Cathodic protection should be used, preferably with automatic control.

To avoid electrolysis damage in the vicinity of the supply point (higher current density) metallic structures should be bonded normally to the negative bus-bar.

9.11 Beneficial Results

The use of steel casing in heat exchangers with copper alloy tubes and tube sheets reduces corrosion of copper metals (see Figure 9.29).

The use of galvanized or metallized steel washers in contact with the anodic member of the connection reduces galvanic attack on this metal (see Figure 9.30).

Sacrificial metals can be used for prevention of stress corrosion cracking (see Figure 9.31) and as protective coatings (see Figure 9.32).

9.12 Shape or Geometry

The embodiment of corrosion control in the design of a product can be achieved most efficiently by capturing this control within the product's geometry, i.e. in its three-dimensional form, its layout, and its relative and spatial positions. There is no other design effort that can assist as much in prevention of corrosion for such a comparatively small outlay.

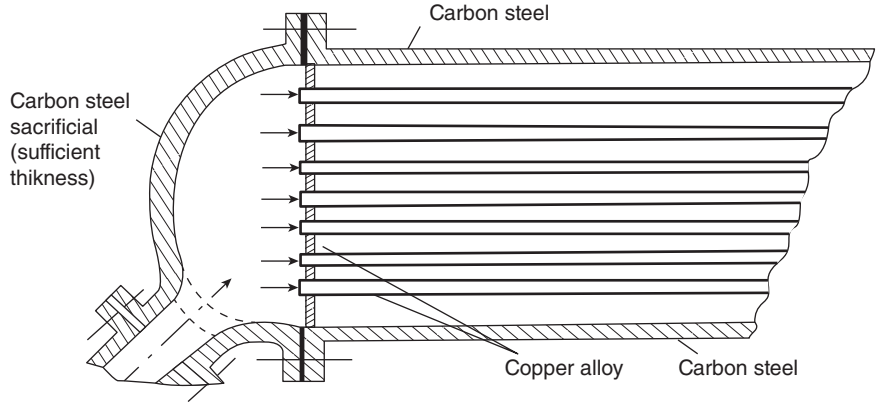


Figure 9.29 *Use of steel casing in heat exchangers with copper alloy tubes and tube sheets to reduce corrosion of copper metals. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

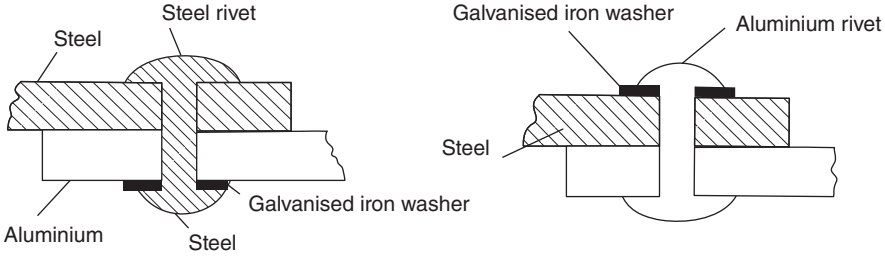


Figure 9.30 *Use of galvanized or metallized steel washers in contact with the anodic member of the connection reduces galvanic attack on this metal. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

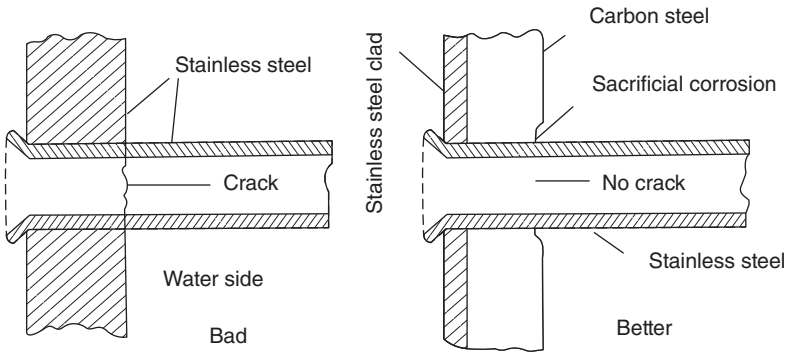


Figure 9.31 *Use of sacrificial metals for prevention of stress corrosion cracking. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

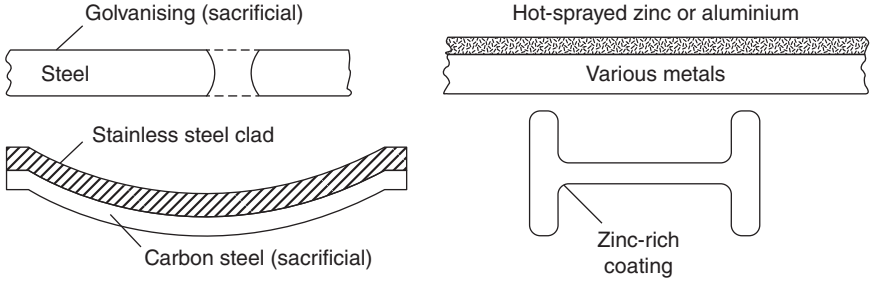


Figure 9.32 *Use of sacrificial metals as protective coatings. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

Whereas the pattern of a utility basically depends on its functional, material, and fabrication requirements, it is within the scope of a good designer to select from the available possibilities only such geometric shapes or combinations of forms that help to reduce corrosion attack in the most efficient and economical manner.

The sole purpose of the following text and diagrams is to indicate some of the possible avenues of approach to the problem of reducing corrosion attack, by a judicious adjustment of the designed form. There is no intention to restrict the designer in the inventive process only to the presented form, provided the interests of corrosion control are duly and effectively represented.

9.12.1 Requirements

The geometry of the designed component should not only be appreciated within the narrowly defined lines of the component itself, in its own splendid isolation; its interdependence with other components within the system, within the utility, and the space generally should also be considered. The form should not be viewed rigidly from any one obvious aspect, the natural one to a respective designer, but from all sides, i.e. including the blind one.

Excessive complexity should be avoided; design should be simple, sleek, and streamlined. All environmental and functional conditions should be made as uniform as possible throughout the entire design system, by application of selective geometry. The outside and inside geometric form, including

the layout and general location, should facilitate the product being kept clean and corrosion-free at all stages of fabrication, assembly, and during service – based on normal operation and breakdown conditions – without excessive effort.

The design should prevent the adverse corrosive influence of one component of the utility on another in various media, due to spillage, emission of fumes or vapor, thermal and chemical effects, transfer of corrosive matter, formation of hot spots, etc., within the selected pattern. Where water can be deposited by rain, spray, or condensation, all reasonable design precautions should be taken to provide free access of drying air to the wetted surfaces. Fast drying of such surfaces should be secured primarily by an appropriate selection of individual shapes, as well as by their proper combination and attachment.

Shapes that, contrary to their function, retain corrosive combinations of air and electrolyte should be avoided. The designed product should neither collect nor retain unwelcome compound corrosive media within their form and frame. Access and retention of unwelcome solid contaminants or waste, which may act within the designed form by absorbence and retention of moisture or by abrasive action, should be avoided by the correct selection of form and arrangement.

The geometry of the product should be designed for exclusion or inclusion of oxygen, as relevant to the requirements of the particular construction material (e.g. active/passive metals require oxygen for the build-up of a protective film; corrosion of other metals or alloys is aggravated by the presence of oxygen).

Design forms should be chosen that lessen the effect or reduce the occurrence of such types of corrosion that depend directly or indirectly on the geometry of the product for their occurrence and degree of aggressiveness. Such shapes, forms, combinations of forms and style of attachment should be selected, whose fabrication, joining technique, and treatment will not aggravate corrosion.

Those geometric forms should be chosen that can assist in securement of optimal results from the selected corrosion preventive measures, at their initial application, and at any future repetitive application.

Where materials that are treated prior to fabrication or assembly are used, a geometric form allowing fabrication and assembly without major damage to the pretreatment should be chosen (Figure 9.33).

Access to corrosion-prone areas should be considered to be of prime importance.

The effect of corrosion on operability and performance of the product at the given geometry should be considered, particularly in areas not subject to periodic examination.

The size and shape of structural members and components should be selected to avoid double dipping or progressive galvanizing – single immersion is preferred.

9.13 Structures

Locate the utility where it cannot be adversely affected by natural and climatic conditions or by corrosive pollution (gaseous, liquid, or solid) borne by prevalent winds or sea and river currents from near or distant sources.

The optimum arrangement and layout within the utility should be selected to prevent adverse effects of one part of the assembly on another (based on normal operation and breakdown conditions). Undrainable traps accumulating liquids and absorbent solid waste should be avoided.

Adequate drainage, scuppers, and limber holes should be provided. Scuppers should be fitted at the lowest possible position in a space to ensure full drainage. Movement should be taken into consideration when choosing the optimum position for a scupper. Self-draining structures should be

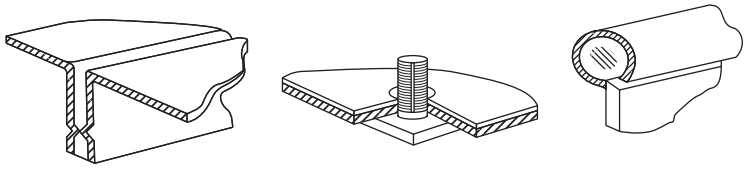


Figure 9.33 *From the left: spot-welded standing seam, projection-welded bolt, reinforced rolled edge. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

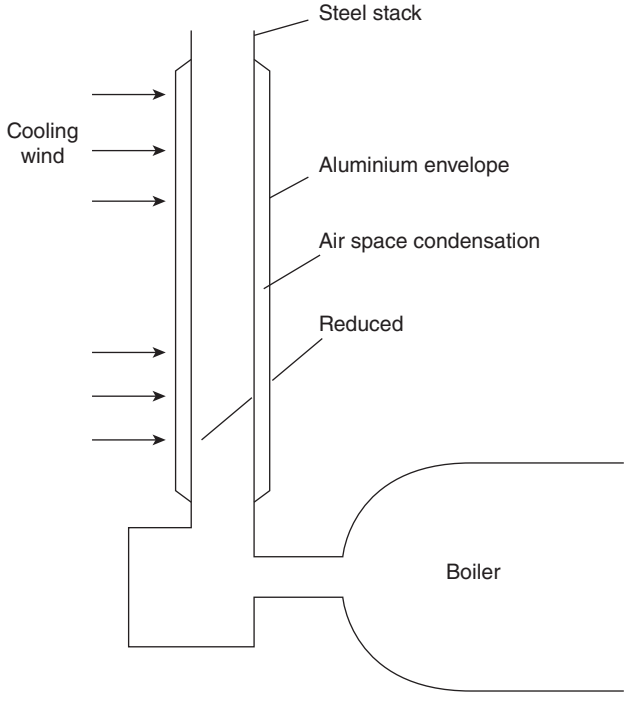


Figure 9.34 *A example of the prevention of condensation in a critical space by selected geometry. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

designed, where possible. Access of abrasives and other solid contaminants to critical spaces should be prevented; selection of the right geometry can prevent condensation (see Figure 9.34).

Where crevices cannot be avoided, precautions should be taken to prevent ingress of corrosion by improving the geometry, fit, or surface texture. Where possible, laps and crevices should be avoided or sealed effectively, especially in areas of heat transfer, between metal and a porous material, or where an aqueous environment contains inorganic chemicals or dissolved oxygen.

Laps should face downwards on exposed surfaces; every effort should be made to give the design a shape or form that will reduce the effect of excessive velocity, turbulence of flow, and formation of gas bubbles (see Figure 9.35).

Sufficient concrete cover should be provided for steel reinforcement in aggressive environments to prevent corrosion of the embedded steel. The arrangement of reinforcement in concrete

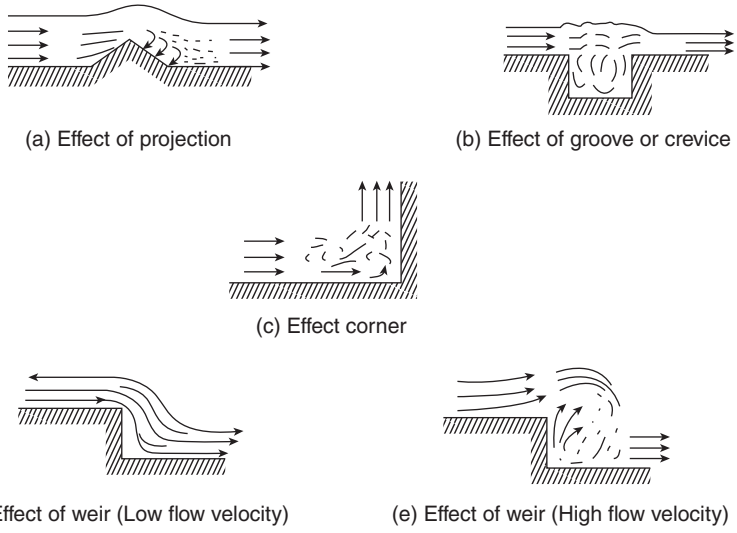


Figure 9.35 *The effects of shape on excessive velocity, turbulence of flow, and formation of gas bubbles. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

should be determined, not only by structural requirements, but also by relevant corrosion-control considerations.

9.13.1 Piping Systems

Piping systems should be designed for an economic velocity of the fluid under consideration (there is no limitation for gases or steam, unless liquids or solids are entrained), unless otherwise necessary. In normal conditions, at velocities of 61–305 cm/s (2–10 ft/s) there should be no severe corrosion in absence of other factors. Relative to piping bores, maximum fluid speeds may vary from a mean velocity of 91 cm/s (3 ft/s), for a 0.95 cm (3/8 in) bore, to 305 cm/s (10 ft/s), for an 20.32 cm (8 in) bore. It should be noted that economic velocity is also governed by the material used.

Higher velocities than those mentioned above may, however, be required to provide a uniform and constant oxygen content in fluids, which is needed for formation of protective films on active/passive metals and those metals that are susceptable to pitting, e.g. stainless steel (austenitic – minimum 152 cm/s (5 ft/s) required), Monel, aluminum alloys, etc.

The removal of rust, debris and other solid contaminants (entrained or formed on stream) from the system should be provided for. Similarly, there should be provision for removal of liquids from compressed air, gas, and steam systems, and entrained air and gases from the liquids in piping systems.

The interior of piping systems should be streamlined for easy drainage (see Figure 9.36):

- Avoid stagnancy-producing stubs and dead ends
- Slope all pipelines (except rising vents) continuously downstream to their outlets or other terminals, if possible, for complete emptying
- Provide drainage in dipped sections of pipes
- Slope elbows for drainage if possible.

Turbulence, rapid surging, excessive agitation, and impingement of fluids in the system should be avoided.

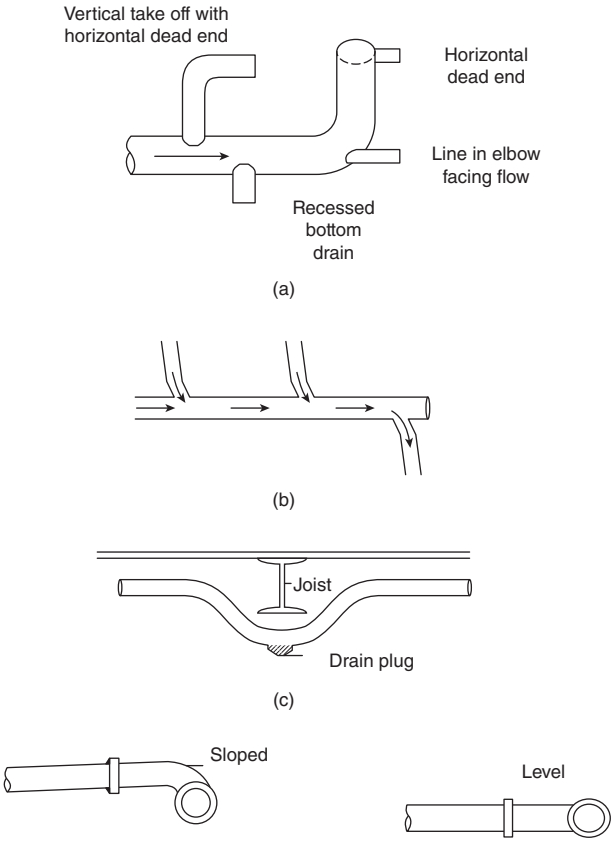


Figure 9.36 *Streamlining of the interior of piping systems for easy drainage. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

For less resistance, a venturi tube is preferable to an orifice plate (Figure 9.37).

Sudden changes (sharp bends) in the direction of fluids in pipelines and fittings should be avoided, especially in those made of lead, copper, and their alloys (see Figure 9.38).

Complete filling of pipelines should be arranged, if possible (see Figure 9.39).

Pressure differences in the pipelines should be equalized (see Figure 9.40).

The system should be designed to keep the absolute pressure as high as possible to restrict the release of gas bubbles. Set the vertical waste heat boilers off at a slight angle. Shape any parts, such as the discharge side of turbines, the suction side of pump impellers, and the discharge side of regulating valves, to avoid low pressure and high turbulence build-up and test the design in a cavitation tunnel.

The bend radii of pipes should be as large as possible. Normally, a minimum of three times the diameter of the pipe should be enforced for economical velocities. This may be adjusted up for various metals, depending on their fabrication difficulties, e.g. mild steel and copper pipe – three times, 90/10 copper nickel – four times, minimum, and high-tensile steel pipe – five times the diameter of the pipe, minimum. Adjustment for high velocities is, of course, also required – the higher the velocity the larger the radius of the pipe. Elbows of similar radii, i.e., minimum three diameters, are advantageous if these are commercially available.

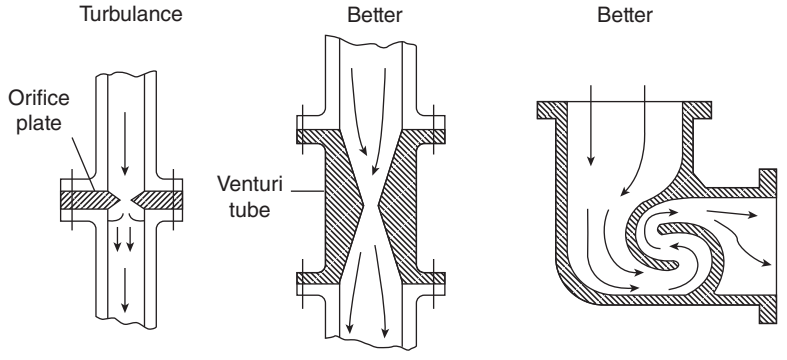


Figure 9.37 *For less resistance, a venturi tube is preferable to an orifice plate. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

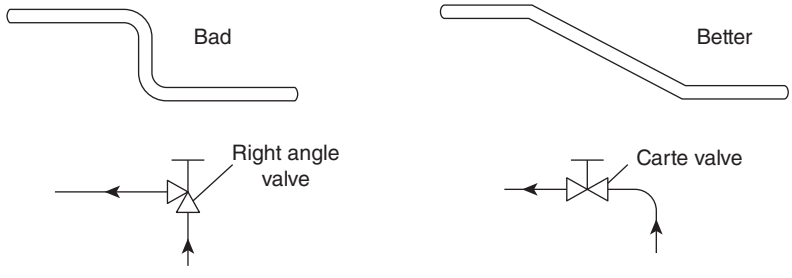


Figure 9.38 *Examples of sudden changes (sharp bends) in the direction of fluids in pipelines and fittings. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

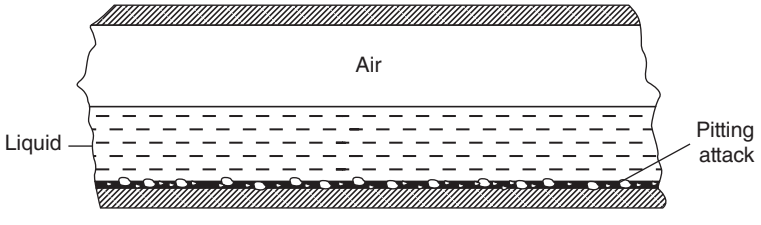


Figure 9.39 *Arrangement for complete filling of a pipeline.*

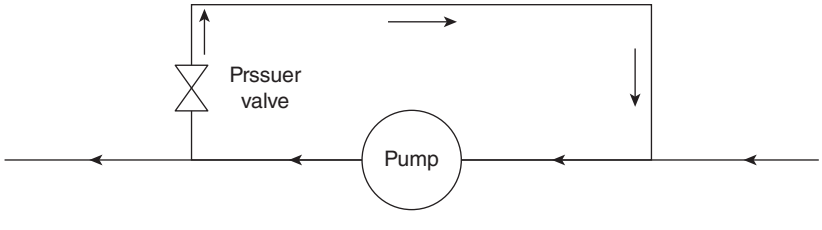


Figure 9.40 *Equalizing pressure differences in a pipeline.*

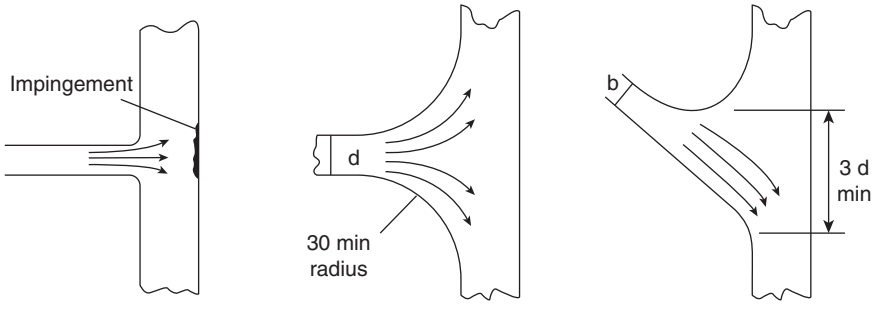


Figure 9.41 *Branching off on high-velocity connections.*

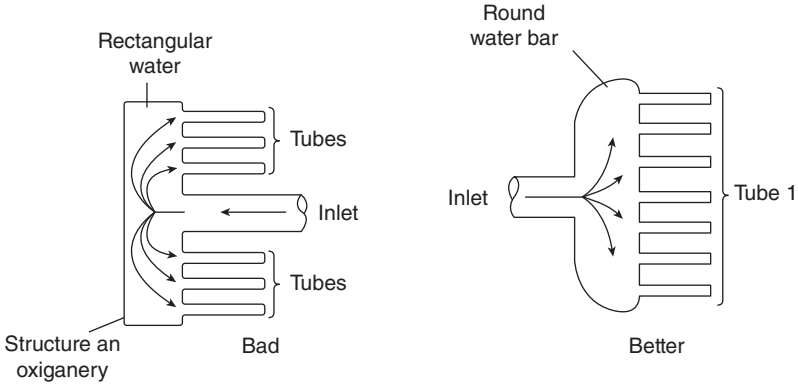


Figure 9.42 *Cooling water starvation at the periphery of a tube bundle. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

Branching off in tees on high-velocity connections should be avoided – laterals are preferred (see Figure 9.41).

Optimal forms of take-down joints that do not cause turbulence should be selected:

- Avoid joints with a possibility of inaccurate and incomplete fitting
- Use flanges, fittings, and gaskets with an equal inside diameter – rate of impingement = squareof maximum joint error in alignment
- Avoid cooling water starvation at the periphery of the tube bundle (see Figure 9.42).

Condensers should be designed for a realistic amount of excess auxiliary exhaust steam, with reasonable velocity steam inlet and exhaust openings. Steam baffles should be angled away from the condenser bracing and other critical spaces.

When discharging directly to the atmosphere, the discharge should not impinge on other piping or equipment.

Plastic piping runs should not be located near high ambient temperature sources, including other piping, ductwork, or conductors. Plastic piping supports should be closer together than for a metal pipe to compensate for the more critical expansion allowance. Formation of hot spots by the

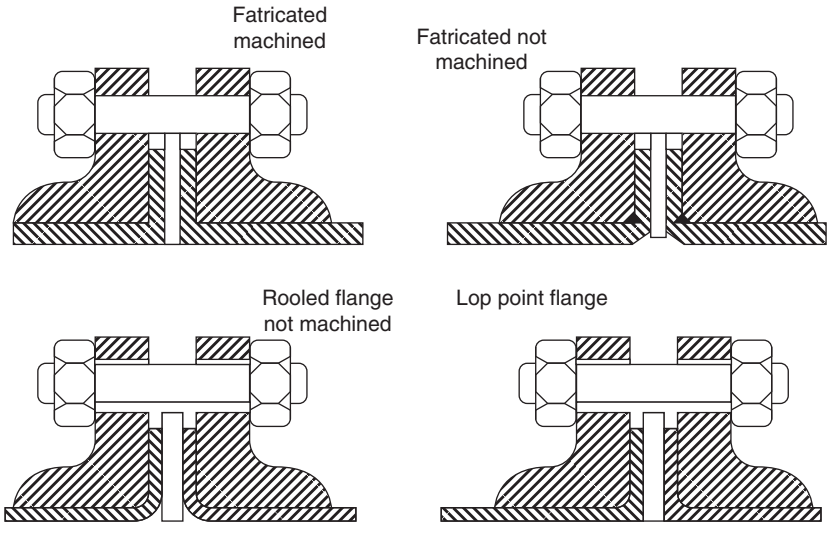


Figure 9.43 *Selection of balanced geometry.*

attachment should be avoided and there should be approximately equal water velocity through all the tubes in the heat exchanger. Balanced geometry to suit materials, fabrication and environmental conditions should be selected (see Figure 9.43).

9.13.2 Tanks and Vessels

- Welded tanks are preferable to those riveted or bolted.
- Fastener joints provide sites for crevice corrosion.
- Secure the flatness of welded plates on tank tops and bottoms during welding.
- Avoid undrainable horizontal flat tops of tanks; where possible provide appropriate drainage. This applies also to underground tanks
- Slope tank bottoms towards drain holes to prevent collection of liquids after emptying of tank.
- Direct inlet pipes towards the center of the vessel.
- Position heaters or heating coils towards the center of the vessel, if possible.
- Prevent crevice corrosion between the seating and the tank.
- Prevent the adverse influence of haphazard insulation and avoid moisture entrapped within it.
- Seal tanks holding hygroscopic corrodants well to prevent contact with damp air.
- Seal tanks completely against uncontrolled leakage of liquids, blowing of air or steam, and dissipation of fumes from the inside outwards and vice versa.
- Avoid conditions that allow absolute pressure to fall below the vapor pressure of the liquid.
- Equalize hydrodynamic pressure differences.
- Provide replaceable impingement plates and baffles where necessary.
- Avoid horizontal bracing in the splash zone.
- Avoid filling tanks with concentrated solutions for dilution purposes along the side walls.

9.14 Mechanics

Any one of the known types of corrosion can lead to damage or breakdown of the mechanical integrity of the designed product; however, stress corrosion cracking, hydrogen damage, corrosion fatigue, and fretting corrosion can result either in a critical, sudden, and catastrophic breakdown of function, or otherwise dangerously reduce the calculated strength of the design materials. Their propagation is closely associated with the product's mechanical strength properties and so a solution to this threat is urgently required and should be of considerable interest to the designers, and to the whole corrosion-control team.

Furthermore, the problems caused by the named types of corrosion are aggravated by the impossibility of timely detection and remedy if an insidious attack occurs largely inside metal or on hidden interfaces; thus there is more or less only one effective solution, that is to take appropriate steps at the design stage for preventive control.

Considering the corrosion/mechanical affinity of the project design, in particular the relationship between the strength of materials and their stress loading under the given corrosive conditions, this appreciation should relate mostly to the tensile stresses (residual or externally applied) arising from the geometry of the component, stresses attributable to fabrication and assembly (including heat treatment and welding), and stresses caused by the operation. The above-mentioned stress loading can be either static or cyclic.

Other forces that can have an adverse effect on the corrosion of materials are those arising from vibration and fluttering, and last but not least the effect of shock should be considered.

Neither of the mentioned corrosion attacks has been ultimately defined by research and, where a critical design or materials are being considered, suitability testing in a laboratory or as a pilot project is recommended. Generally it may be said that, given the right environment, none of the metals or alloys used is completely free of the danger of stress corrosion, except, perhaps, those in a pure form. Some of the most susceptible alloys are those normally selected for highly loaded and critical applications, and it is known that present-day demands on the available strength of materials are supporting this trend. Many failures attributed to the fatigue of metals, overloading, or other physical causes are, in fact, caused by stress corrosion.

Non-metallic materials also suffer from phenomena similar to stress corrosion, e.g. the presence of moisture lowers the strength of glass, stressed plastics crack when exposed to specific organic solvents, etc.

The analysis of corrosion associated with mechanical strength will naturally be very closely related to the appreciation of the prime engineering function and optimization of the designed product. Furthermore, one can qualify it as a functional analysis with a slant towards corrosion-control appreciation. Mechanical fault can initiate or aggravate corrosion incidence and corrosion per se can initiate or cause catastrophic failure.

Whilst an engineering product can fail due to stress, fatigue, or friction in a benign corrosion environment, unless absolute perfection has been reached in design and fabrication through strict attention to the good practices of secure mechanical design, these optimal conditions are only very rarely obtained in practice. It is truly advisable to pursue the sound policy of parallel appreciation of functional engineering and corrosion-control parameters by mutual consultancy to secure a safe product.

This section claims a reasonable chance to advise, indicate, and initiate some of the possible ways and means to reach a common denominator between the designers and corrosion specialists in their endeavor to secure a safe design, and to assist either of the concerned parties in their recollection of the selective factors involved.

9.14.1 Requirements

Materials, stress levels, environment, service temperature, and design life are important parameters and should be considered in every design.

Stress corrosion cracking is affected only by tensile stresses (residual or externally applied); purely compressive stresses do not cause stress corrosion cracking and none will occur with elastic stresses.

The correct materials should be selected. If possible metals and alloys susceptible to stress corrosion or corrosion fatigue should not be specified for highly loaded and critical structures and equipment in malignant corrosive environments.

Preference should be given to materials that are resistant both to intergranular and stress corrosion, especially for applications involving residual and induced stresses. Alloys that are normally most resistant to intergranular corrosion are also more resistant to stress corrosion.

Metals susceptable to hydrogen embrittlement should be avoided in critical structures and equipment.

Any selection of dissimilar metal couples, if absolutely necessary, should be confined to compatible couples in environments leading to stress corrosion cracking, corrosion fatigue, and fretting corrosion.

Within the requirements of the economic life of the product, adequate control of heat treating and metal working processes is required to develop microstructure optimally resistant to a specific environment.

All bending, forming, and shaping should preferably be performed on metal in an annealed condition, and every effort made to use the lowest practicable stress level.

Specify metal working, heat treating, flame and induction hardening, case hardening, carburizing and nitriding (grain size refinement, metallurgical phase transformation, strain, and dispersion hardening), whichever is required for increase of local strength or for improvement of fatigue strength or for introduction of compressive residual stresses into one or both of the rubbing surfaces.

Carbide solution treatment of corrosion-resistant steels should be specified to minimize sensitivity to intergranular corrosion. Suitable stress relieving measures (heat treatment, surface treatment, ultrasonic oscillators) should be specified.

Select welding techniques that can produce sound welds. Defects (selective precipitation of phases, gas pockets, laps, undercutting, non-metallic inclusions, metallic alloying with prefabrication primers and other surface coatings, fissures, and cracks) can act as sites of high residual tensile stress and thus lower the corrosion resistance. The chemical and metallurgical composition of welding rods should be compatible with the base metals, especially in the case of high-strength metals.

Select and specify appropriate welding rods and welding techniques that will not cause hydrogen embrittlement of high-strength metals.

Careful and optimal preparation and finishing of welds for stressed structures and equipment is imperative.

For prevention of stress corrosion cracking observe the precautions:

- Minimize applied or residual tensile stresses
- Secure sufficient flexibility
- Increase size of critical sections
- Reduce stress concentration or redistribute stress
- Compensate for loss of stiffness produced by penetration
- Avoid misalignment of sections joined by riveting, bolting, and welding

- Design simple joints under stress; avoid lap welding, riveting, bolting; but or fillet welding is preferred
- For stressed structures specify techniques that produce sound welds; also careful preparation and finishing of welds
- Specify and design for elimination of stress raisers
- Select suitable material (metallurgical composition)
- Avoid specifying any machining, assembling, or welding operations that impart residual tensile stresses
- Use materials in assembly with similar coefficients of expansion
- Secure control of heat treatment and metal working to develop a resistant microstructure
- Specify input of compressive surface stresses by suitable treatments
- Specify electroplating or metallizing in stressed areas
- Select suitable surface coatings; specify passive surface films, suitable organic coatings, or staved resin coatings in critical areas
- Use controlled cathodic protection
- Analyze and control environmental conditions; exclude corrosive environments (see Table 9.2)
- Secure maintenance of low service temperatures
- Eliminate possible corrodants from service environments or suitably inhibit
- Prevent by design repetitive wetting and drying of critical surfaces
- Prevent all types of corrosion in critical spaces by any suitable means
- Conduct stress analysis using suitable computer software to determine stress concentration and distribution
- Avoid stress corrosion cracking under thermal insulation.

Table 9.2 *Environments causing stress corrosion*

Material	Environment
Aluminum alloys	Water and steam; NaCl, including sea atmospheres and waters; air, water vapor
Copper alloys	Tropical atmospheres; mercury; $HgNO_3$; bromides; ammonia; ammoniated organics
Aluminum bronzes	Water and steam; H_2SO_4; caustics
Austenitic stainless steels	Chlorides, including $FeCl_2$, $FeCl_3$, NaCl; sea environments; H_2SO_4fluorides; condensing steam from chloride waters; H_2S
Ferritic stainless steels	Chlorides, including NaCl; fluorides; bromides; iodides; caustics; nitrates; water; steam
Carbon and low-alloy steels	HCl; caustics; nitrates; HNO_3; HCN; molten zinc and NaPb alloys; H_2S,H_2SO_4; HNO_3; H_2SO_4; seawater, bicarbonate, carbonate
High-strength alloy steels (yield strength 1380 kPa plus)	Sea and industrial environments
Magnesium	NaCl, including sea environments; water and steam; caustics; N_2O_4; rural and coastal atmosphere; distilled water
Lead	Lead acetate solutions
Nickel	Bromides; caustics; H_2SO_4
Monel	Fused caustic soda; hydrochloric and hydrofluoric acids
Titanium	Sea environments; NaCl in environments 288 °C (550 °F); mercury; molten cadmium; silver and AgCl; methanols with halides; fuming red HNO_3; N_2O_4; chlorinated or fluorinated hydrocarbons

Stress corrosion cracks grow in a plane perpendicular to the operating tensile stress, irrespective of its nature (applied or residual), so appropriate precautions should be taken in design.

Control the stress level by design. Time to failure depends on stress level, i.e. it tends to decrease rapidly as stress increases into a range of 50–90% of yield strength. Laboratory data, however, are not always reliable in practical conditions. Uncontrolled stress corrosion cracking could occur at stress levels considerably below the yield strength, but active stresses would have to be great enough to cause some plastic strain (creep strain might be sufficient).

Note: Corrosion within stress cracks can develop pressure up to 1.55 kgf/mm^2 (1 ton/inch^2).

For prevention of hydrogen embrittlement, observe precautions and preventive measures as follows:

- Select a clean metal
- Select a resistant material, homogeneous or clad
- Select low-hydrogen welding electrodes and specify welding in dry conditions
- Select correct surface preparation and treatment
- Avoid incorrect pickling and plating procedures
- Metallize with resistant metal, or use a clad metal
- Induce compressive stresses
- Remove hydrogen from metal by baking at 93–149 °C (200–300 °F)
- Provide for control of media chemistry (e.g. use inhibitors, remove sulfides, arsenic compounds, cyanides, and phosphorus-containing ions from the environment)
- Control cathodic protection potential
- Specify impervious protective coating (e.g. rubber, plastic)
- Avoid anodic metallic coatings.

For prevention of corrosion fatigue observe precautions and preventive measures as follows:

- Minimize or eliminate cyclic stressing
- Increase size, bulk, or local strength of critical sections
- Reduce stress concentration or redistribute stress
- Streamline fillet design for decrease of stress concentration and improvement of stress flow
- Select the correct shape of critical sections
- Size components by exchange of useless material in non-critical components for stronger critical sections
- Provide for sufficient flexibility to reduce overstressing by thermal expansion, vibration, shock, and working of the structure or equipment.
- Provide against rapid changes of loading, temperature, or pressure
- Avoid fluttering and vibration-producing or vibration-transmitting design
- Increase natural frequency for reduction of resonance corrosion fatigue
- Improve ductility and impact strength
- Specify stress relief by heat treatment or by shot peening, swaging, rolling, vapor blasting, tumbling, etc., to induce compressive stresses
- Specify asuitable surface finish
- Specify and design for elimination of stress raisers, fretting, scoring, and corrosion
- Specify electrodeposits of zinc, chromium, nickel, copper, or nitride coatings by plating techniques that do not produce tensile stresses
- Select a suitable surface coating
- Change or inhibit corrosive environment
- Balance strength and stress throughout the component (see Figure 9.44).

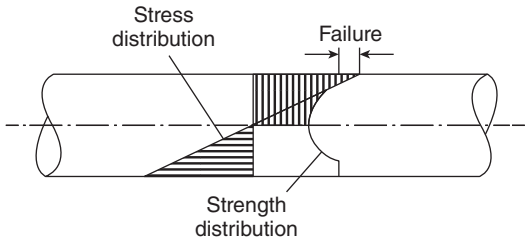


Figure 9.44 *Balance strength and stress throughout a component.*

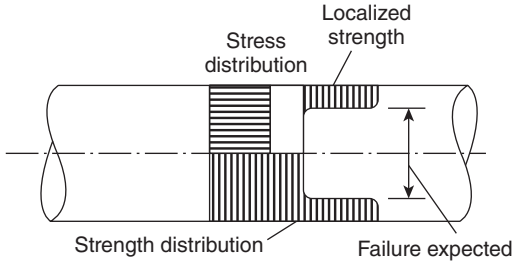


Figure 9.45 *Influence of stress distribution, for a given strength distribution, on the fatigue life of the product. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

- Evaluate influence of stress distribution, for a given strength distribution, on the fatigue life of the product (see Figure 9.45).Streamline fillets for various types of loading to obtain a decrease in stress concentration and to improve the stress flow.
- Avoid deformation of materials round welds, rivets, bolt-holes, press fits or shrink fits.

For prevention of fretting corrosion observe precautions and preventing measures as follows:

- Avoid vibration-transmitting design
- Introduce barrier between metals that allows slip
- Increase load (but do not overload) to stop motion
- Select suitable materials
- Specify protective coating of a porous (lubricant-absorbing) material
- Isolate moving components from the stationary ones
- Increase abrasion resistance between surfaces, by treating one or both of the surfaces
- Design for exclusion of oxygen on bearing surfaces
- Select compatible materials
- Improve lubrication design arrange for better accessibility
- Make arrangements for flushing of debris by the motion of lubricant
- Select a suitable lubricant.

Allow for differential expansion and pressure differentials. Select design for correct and exact fitting (note expansion and contraction of metals and strain creep). Forcing one part through the other and subjecting components to excessive local stress can cause adverse corrosive conditions.

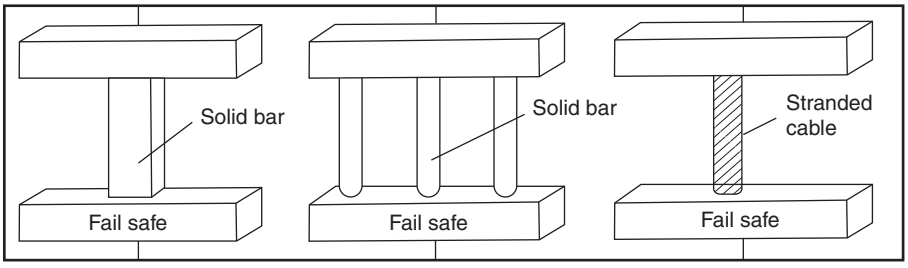


Figure 9.46 *Set design allowable stress to minimize the rate of fatigue damage in service. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

In the absence of a corrosive environment the magnitude of stress is considerably below the level causing damage. Identify corroding componants (e.g. chlorides) and design for their removal, reduction, or elimination even if the quantity is small, especially from the critical areas, if possible.

Stress corrosion cracking or corrosion fatigue may occur even in humid air or other mild corrosives. Prevent intermittent wetting and drying of critical surfaces if possible.

Fatigue strength increases in vacuum or inert atmospheres. Oxygen and water vapor contribute to corrosion. Increasing the intrinsic fatigue strength of a material may not improve the fatigue corrosion behavior as much as an optimal zed environment.

Set design-allowable stress that will minimize the rate of fatigue damage in service (see Figure 9.46).

9.14.2 Structures

- Provide in the design for sufficient flexibility of structures to prevent over-stressing by thermal expansion, vibration, and working of the structures
- Avoid riveted assemblies, which can be subject to vibration
- Stress analysis of complex structures by computer is recommended
- Structural members in direct tension or compression are preferred to those subject to bending and torsion
- Reduce the stress concentration factors in the structure as much as possible
- Size and position the members within the structure to carry distributed loads; the smaller the member, the better it can distribute the stress
- Provide generous fillets at internal and external corners
- Balance the stiffness; relative stiffness, where each member carries its share of load, improves the strength (see Figure 9.47).Minimize expansion and contraction of structural members (creep-, thermal-, or stress- induced); select materials having similar coefficients of expansion
- Deformation and cold working of metals, especially those containing carbon and nitrogen, may promote preferential local attack at imperfection sites and increase the corrosion rate; stress relief is indicated.
- Defects (gas pockets, laps, undercutting, non-metallic inclusions, fissures, and cracks) can act as sites of high residual tensile stress and can lower the corrosion resistance of the structure
- Avoid notches; the only structural materials insensitive to notches are reinforced plastics
- Avoid sharp edges (especially feather edges), specify chamfering, removal of burrs by grinding, milling, or peening; avoid sharp re-entrant corners

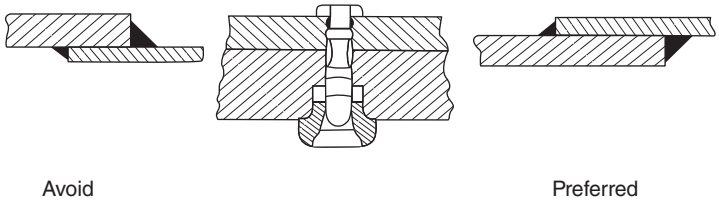


Figure 9.47 *Balancing the stiffness. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*



Figure 9.48 *Avoid intermittent welds.*

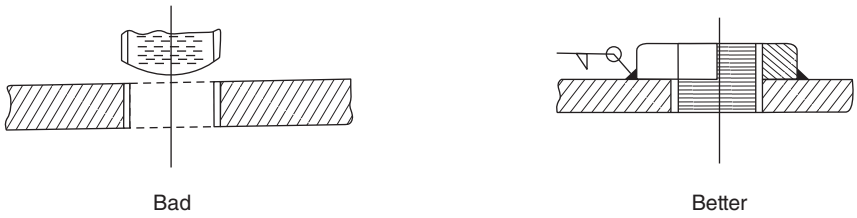


Figure 9.49 *Avoid tapped holes.*

- A design allowing the exact assembly and fitting of individual members or units without undue stressing of one part by the other is preferred
- Parts penetrating or interfering with the main structure should withstand the same hydrostatic pressure and deformation loading as the main structure
- Lateral stiffeners should be as large as possible or practicable
- Simple welded joints are preferred to those riveted or bolted for attachments subject to stress loading; butt and fillet welding is preferred to lap or spot welding
- Avoid intermittent welds (see Figure 9.48)
- Avoid tapped holes (see Figure 9.49).
- Where fretting corrosion between structural members subject to vibration could arise:
  - Separate rubbing surfaces by shims or inserts (rubber, plastics)
  - Design for use of flexible arms.

- Protect against stress corrosion of prestressed reinforcement in concrete by careful reduction of stress, by elimination of corrosion through good concreting practice, and by appropriate protection of embedded steel. Note: Protect reinforcement cables awaiting full stressing and grouting.

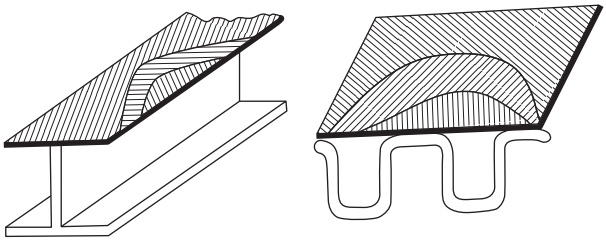


Figure 9.50 *Unsuitable metals can be replaced with next-generation filament-wound composites. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

- Use of cathodic protection (sacrificial or impressed) to restore endurance limit in stress of high strength steels is appropriate only if the following conditions are met:
  - The cyclic stress varies from tension to an equal value in compression
  - The cyclic rate is fast – at least many hundreds of cycles per minute
  - The over-polarization of metal through excessive development of hydrogen is avoided.
- Eliminate, if possible, corrodants in the service environment, or use corrosion inhibitors.
- Pipe purchased for fabrication and galvanizing should be ordered without mill scale, or the mill scale should be removed by blast cleaning prior to pickling.
- In a design permitting unsuitable metals, they may be replaced with next-generation filament-wound composites (e.g. continuous), glass, graphite, boron, beryllium, titanium alloy, steel, carbon, silicone filament, or strip unidirectional, bidirectional, multi-directional (see Figure 9.50).

9.14.3 Equipment

- Machinery and equipment in a corrosion-prone environment should be mounted on seatings as stiff as is functionally possible, with differing resonant frequencies from the forcing frequencies initiated by the machine or equipment
- Where the equipment is mounted on tubular seating, the seating should be in tension or compression
- Provide in the design of equipment supports for sufficient flexibility and reduce stress concentration
- Where two structures (pipe systems, electrical conductors, ventilation ducts) can deflect relative to each other under shock loading, equipment subject to corrosive conditions should not be attached rigidly to both (see Figures 9.51 and 9.52).
- In high-speed, high-performance equipment subject to corrosion and resonance fatigue failure, all component members, parts, or groups should be considered together as one assembly, for prevention of bending stresses due to lateral vibration. The required lateral stiffeners should be as large as practicable.
- Maximum reliability of equipment is attained when all components have the same factor of safety, whatever their modes of fatigue.
- Improve fatigue strength by elimination of fretting and scoring.

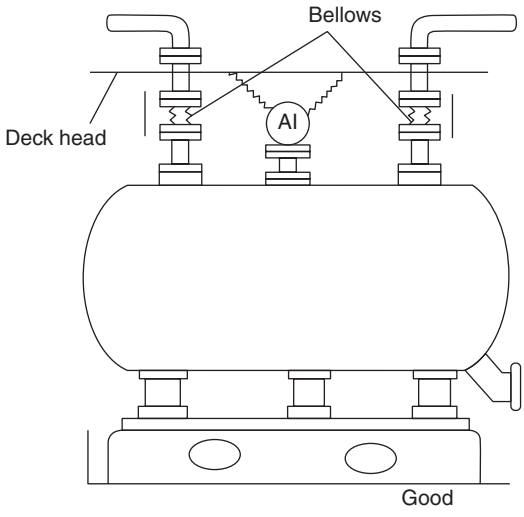


Figure 9.51 *Equipment subject to corrosive conditions should not be rigidly attached to two moveable structures. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

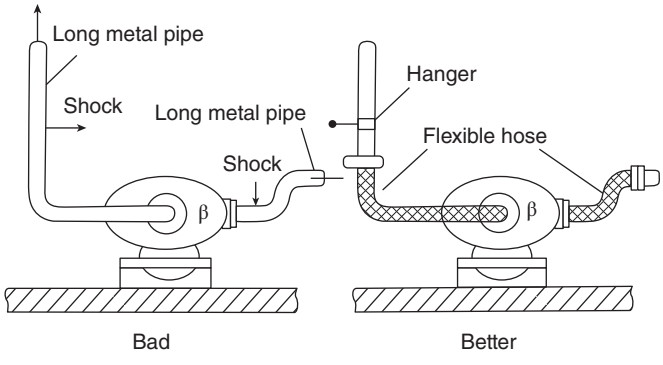


Figure 9.52 *Equipment subject to corrosive conditions should not be attached rigidly to two pipe systems. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

- Any compatible means of stopping corrosion will improve fatigue strength.
- Fibre-bonded plastics used as separators in bushes and bearings immersed in seawater can assist in reduction of fatigue failure incidence.
- Gaskets used for absorption of vibration can help to reduce the probability of fretting corrosion.
- Take precautions to avoid fretting corrosion between component surfaces and shims fitted in between (e.g. shims between the bed plate and the top plate of a diesel engine).

9.14.4 Piping Systems

- Piping systems can be adversely affected by thermal expansion, shock, vibration, and working of the structures.
- Provide for sufficient flexibility of piping to prevent pipe movements from causing overstressing and failures from stress corrosion cracking of pipe materials or anchors, leakage at joints, or detrimental distortion of connected equipment through excessive thrusts and movements:
  - Change direction through use of bends, loops or offsets.
  - Provide for absorption of thermal movements by utilizing expansion, swivel, or ball joints, corrugated pipe, or flexible bellows.
- Avoid, in corrosive conditions, an imbalance in strain concentrations of weaker- or higher-stress portions of pipe systems produced by:
  - Use of small pipe runs in series with larger or stiffer pipes and smaller lines, relatively highly stressed.
  - Use of a line configuration, in a uniform size pipe system, for which the neutral axis or thrust line is situated close to the major portion of the line itself, with only a very small offset portion of the line absorbing most of the expansion strain.
  - Local reduction in size or cross-section, or local use of weaker materials.
- Where expansion joints are subject to a combination of longitudinal and transverse movements, both movements should be considered.
- Anchors, guides, pivots, and restraints should be designed to permit the piping to expand and contract freely in directions away from the anchored or guided point.
- Hanger rods and straps should allow free movement of piping caused by thermal expansion and contraction, and physical working of the supporting structure.
- Sway braces or vibration dampeners should be used to control the movement of piping due to vibration.
- Piping joints should not be located at points of maximum stress, such as those produced by the lever action of long flexible pipes or equipment.
- Where critical stresses are expected, an appropriate geometry of pipe fittings should be selected. If such fittings are not available, these areas should be adequately reinforced.
- Take-off connections should withstand all stresses in the piping system, including those induced by cyclic loading.
- Thermal shock to steam lines by contact with cold condensate return lines should be prevented by either lagging in take-off connections with the steam main, or lengthwise metallic contact between the two parts.
- Round or oval ducts are stronger and stiffer than rectangular ones and therefore more effective in reducing vibration stresses.
- A pulsating pipe penetrating a non-watertight bulkhead should be passed through a cut hole 1.3 cm (0.5 inch) oversize, and the clearance sealed with a sealing compound.
- A pulsating pipe penetrating a watertight bulkhead should be designed for bolting a resilient rubber, together with gasket, into a close-fitting hole in the bulkhead.
- Pipes conducting liquids with noticeable fluctuations of pressure (e.g. pump impulse) should be provided with flexible pipe hangers throughout the length of the system.

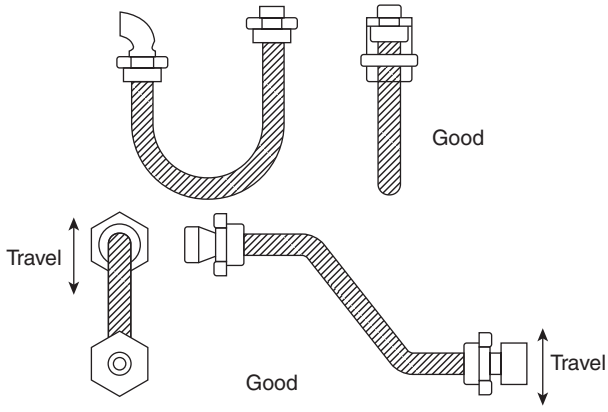


Figure 9.53 *Avoid subjecting flexible hose to torque by twisting on installation or on flexure in corrosive conditions.*

- Risers passing through decks should have adequately liberal expansion bends to absorb the part of the stresses imposed by shock.
- Hangers, straps, and supports should be adequately engineered and positioned to dampen, absorb, or distribute any critical shock loading of the relevant pipe system within, or occasionally outside, the operating parameters.
- Flexible hose can provide against stresses caused by the following motion problems:
  - Piping misalignment
  - Vibration and shock
  - Reciprocating motions
  - Random motions
  - Thermal expansion and contraction.
- Avoid sharp bends on flexible hose in corrosive conditions.
- Avoid subjecting flexible hose to torque by twisting on installation or on flexure (specify) in corrosive conditions (see Figure 9.53).
- Snake underground plastic pipe in the trench to compensate for expansion and contraction.
- Where a valve installed in acontinuous piping system is large and heavy compared to the piping itself, it is acceptable to support the valve by securing the piping adjacent to the valve.
- Regulating valves, which project 30–60 cm (1–2 ft) from the pipe system in which they are installed should be supported to cater for athwart-ship shock stresses.
- Valves located at the end of a pipe shall be supported by the valve flange vertically and athwart-ship to the nearest beam of the structure.
- Correct geometry of attachment between heat exchanger tubes and their tube sheet will assist in reducing stress concentration.

9.14.5 Vibration Transfer

- To minimize resonance corrosion fatigue, reduce vibration and fluttering on stressed structures or equipment in corrosive environments:

  - By vibration-damping design of mounting (e.g. sand-filled columns, etc.); inclusion of splinter silencers; lining with absorbent materials; application of damping coatings.
  - By reduction of excitation magnitude-change of frequency (i.e. increase of natural frequency for reduction of resonance corrosion fatigue); regulating the stiffness of structures (e.g. increase of the amount of inertia of cross-section by using beads, ribs and flanges, using I, round or square hollow sections, etc.); modifying the mounting conditions by using angle braces to simulate built-in supports, rather than using the simple (pivotal) supports.
  - By redistribution of mass.
  - By reduction of effective length of a member by mounting struts parallel to the direction of vibratory motion.
- Vibration of equipment should be reduced or eliminated at its source.
- Ventilation trunking should be so routed that compartments with a higher difference of resonance are not directly connected.
- Provide for installation of acoustic hoods where required.
- Avoid cavitation fatigue in engine cooling systems:
  - Investigate and check for probable focal points of vibration in vicinity of vital components.
  - Investigate resonant frequency of the specified materials.
  - Select components made in material of higher fatigue resistance and with the ability to work harden in cold-working actions caused by cavitation.
  - Reduce dispersed air contents in fluid (bubbles 50 μm diameter).
  - Inject, or generate within the system, larger size air or inert gas bubbles to buffer the mechanical cavitation process.
  - Prevent contamination of fluid by cathodic metals and corrosive agents (e.g. chlorides).
  - Inhibit the fluids and eventually use oxygen scavengers.

9.14.6 Surface Treatment (from a Mechanical Point of View)

- Specify uniform and, in critical areas, top grade cleaning of surface.
- Specify removal of oxidized, contaminated, or decarburized surface layers.
- High-strength steels should not be acid cleaned (except anodically) nor cathodically cleaned in an alkaline bath. Select a cleaning method that does not interfere with the mechanical strength of a particular material in a given environment.
- Specify for avoidance of deep surface finish marks in production (or select appropriate fabrication technique) to avoid formation of stress raisers.
- To improve fatigue strength, specify machine finishing with moderately light cut, gentle grinding, abrasive tumbling, etc.
- Reduce mean stresses by specifying input of compressive residual stresses at the surface of a component by work hardening (i.e. by shot peening of stress concentrators and surfaces, by rolling of fillets, grooves, and other surfaces, by vapor blasting, tumbling, burnishing, and chemical peening).
- Specify for application of surface finishes and coatings by techniques that do not produce tensile stresses nor cause hydrogen embrittlement.
- Metal deposition (vacuum deposition, mechanical plating, metal spraying, or electroplating in low hydrogen-producing plating baths) of stressed areas enhances the mechanical strength of metals. Zinc deposition can be considered for steel, metallizing with zinc or commercially pure aluminum for steel or aluminum alloys.

- Electroplating with tin, cadmium, chromium, nickel, or zinc can increase the fatigue strength of metals.
- Application of passive films can in some cases reduce the probability of stress corrosion cracking. Conversion coatings may help to protect surfaces against initiation of stress corrosion cracking and eventually reduce the requirement for more costly remedies (annealing, shot peening, etc.).
- A suitable increase in the coefficient of friction (e.g. roughening of surfaces) can reduce the occurrence of fretting corrosion.
- The use of phosphate coatings (e.g. parkerizing) or porous metallic or inorganic coatings, in conjunction with low-viscosity, high-tenacity lubricants, can help to reduce fretting corrosion, observing that the lubrication arrangements should be made accessible, and flushing of debris by motion of lubricant facilitated.
- Any efficient and compatible painting system applied, where possible, on stressed structures or equipment should reduce the probability of initiation of stress corrosion cracking or fatigue corrosion. Corrosion should be prevented in all critically stressed components by all available means, including surface coatings.
- Coating the surfaces with organic coatings after case hardening, mechanical work hardening, or metallizing brings about improvement in resistance to stress corrosion cracking and in fatigue strength.
- Priming with a chromate primer containing not less than 20% zinc chromate should be specified for all fully heat-treated alloys.
- The use of metallic, inorganic, or organic coatings and linings in steel vessels where hydrogen embrittlement can occur is conditionally recommended, provided these vessels (or structures) are not fabricated of high-strength steels, the structures are not under high stress loading and the coating does not contain reactive zinc or another metal that under specific environmental conditions could react electrochemically whilst development of gaseous hydrogen takes place.
- Steel, clad with austenitic stainless steel or nickel, can also be specified in an environment promoting hydrogen embrittlement.
- Addition of selective inhibitors to the relevant surface environment can reduce the probability of stress corrosion, corrosion fatigue, and fretting corrosion.
- The use of wide radii bends in corners of components for hot dip galvanizing is recommended – this minimizes local stress concentration.
- Whilst continuous sealed welds are preferred for hot dip galvanized components, whenever these are not practical, staggered welding techniques should be specified to reduce thermal stresses.
- The assemblies that are to be galvanized should be preformed accurately to avoid using force to bring them into position.
- Welds should be stress relieved before galvanizing.

9.14.7 Electrical and Electronic Equipment (from a Mechanical Point of View)

- Select materials resistant to intergranular corrosion and stress corrosion cracking, where residual and induced stresses could affect the safe function of the equipment.
- Where metals are to be bent, formed, or shaped, materials that are in an annealed condition should be used.
- Avoid, where necessary, metals subject to hydrogen embrittlement from acid cleaning or plating, or use low hydrogen-producing plating baths.
- Specify relief of embrittlement immediately after plating for a minimum of three hours at 190°C ± 14°C.

- Specify the mechanical stress relief of parts prior to plating (shot peening).
- Specify appropriate preservation with organic coatings, vacuum deposition, mechanical plating, metal spraying, or other processes not producing hydrogen; this in preference to electroplating or chemical plating, where possible.
- Support lighting fixtures on resilient mounts, where possible.
- Avoid rigid attachment of electrical equipment subject to corrosive conditions that can deflect relative to the conductors, whilst such equipment can vibrate or is exposed to shock loading.

10

Surface Preparation, Protection and Maintenance

10.1 Surface

This section covers the interaction between the chosen materials of the substrate and their geometry, on the one hand, and optimum local surface conditions on the other. These surface conditions are developed to benefit both functional fulfillment and corrosion control, and close co-operation between design engineers, corrosion specialists, and technical experts in individual fields of surface-treatment technology is highly recommended.

The optimal configuration, cleanliness, preparation, texture, and pretreatment of internal and external surfaces, and their electrical or electrochemical stability in any of the expected environmental conditions, can considerably enhance the effectiveness of rationalized corrosion control in design. Furthermore, considering that corrosion usually originates at the surface, it is prudent to give high priority to establishing appropriate and definitive surface parameters at the design stage.

10.1.1 Requirements

Simple compact, smooth surfaces, optimally shaped, positioned, and angled are preferred to haphazardly complex and rough-textured configurations of planes, which are prone to accumulation and retention of dust, debris, and moisture, cause difficulties in rendering the requisite anti-corrosion precautions, which are affected by adverse phenomena such as impingement, turbulence, gas-bubble formation, and the creation of concentration cells. Rounded contours and corners provide the best continuity of surface and are preferred to surfaces forming sharp angles.

Hydrodynamically shaped surfaces are favored in flowing seawater and other corrosive liquids, and aerodynamically shaped surfaces in the atmosphere and corrosive gaseous environments, especially at high velocities.

Unless multi-form surfaces are required for other important reasons, flat surfaces are generally preferable; a random combination of surface planes complicates corrosion control (see Figure 10.1). Flexing surfaces should be avoided as much as possible.

Corrosion and Materials Selection: A Guide for the Chemical and Petroleum Industries, First Edition. Alireza Bahadori.
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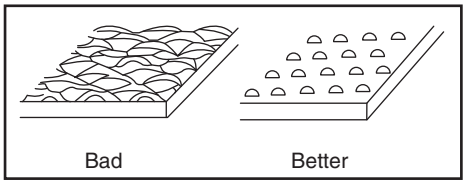


Figure 10.1 *Hydrodynamically shaped surfaces for flowing corrosive liquids.*

Both solid and hollow geometrical bodies are bound to have a number of surfaces and each of these could be exposed to environmental conditions with different corrosive potentials. Separate evaluation may be required for each variant. Critical surfaces, such as welds or surfaces subject to high stress loading, should not, if possible, be contained in spaces difficult to access or in areas where water can lodge (see Figure 10.2).

The continuity of profile flow can be further secured with the help of the following design precautions:

- Reduction of crevices (see Figure 10.3), grooves, and faying surfaces to a necessary minimum.
- Judicious selection of open or closed joints (see Figure 10.4).
- Arrangement of crevices and grooves for self-draining (see Figure 10.5).
- Complete sealing of crevices – including all edges to prevent moisture seeping around them – with suitable plastic materials or inhibited jointing compounds. Seal after the surfaces to be mated have been primed with inhibitive paint (e.g. zinc chromate primer). Crevices between components, at least one of which is stainless steel, may be sealed with petroleum jelly, approved anti-seize and separation compound (high temperature), or other compatible sealant
- Metals depending on formation of surface films for their anti-corrosion properties (stainless steels, nickel alloys, etc.) require the designer's attention to the following surface parameters:
  - Beneficial conformation of surfaces.
  - Continuity of profile flow.

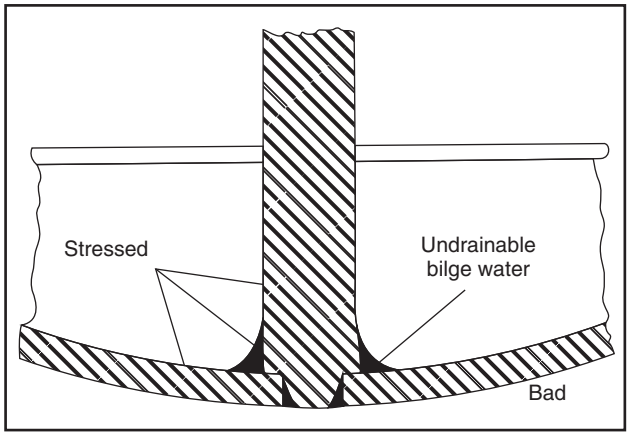


Figure 10.2 *Critical surfaces, such as welds or surfaces subject to high stress loading. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

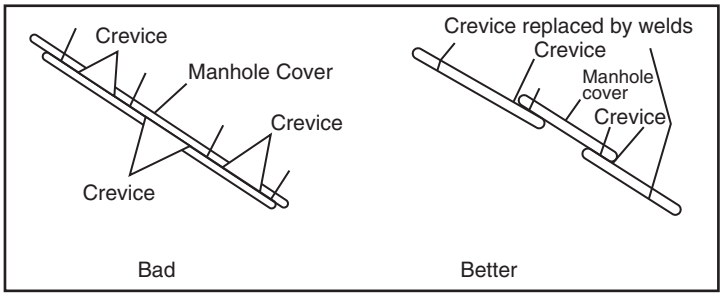


Figure 10.3 *Reduction of crevices to a necessary minimum. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

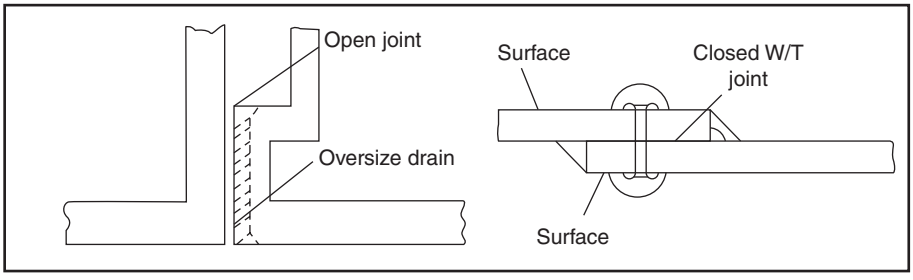


Figure 10.4 *Judicious selection of open or closed joints.*

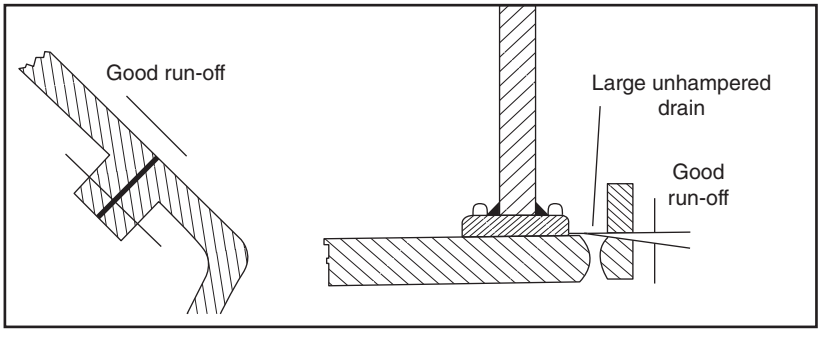


Figure 10.5 *Arrangement of crevices and grooves for self-draining. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

- Total cleaning of surfaces as a preparation for formation of uninterrupted oxide film.
- Uniform pre-treatment of surfaces, if required, including those surfaces which eventually may be confined within the surface discontinuities.
- Significant accessibility of reactive oxygen contained in the operating medium to form and maintain the sound protective surface film.

- In the design, the designer should develop a collection of such surfaces as are electrically stable in the relevant conductive medium. The ideal is the ultimate elimination of a concentrated adverse

effect of one part of the bare or coated surface on the other parts of the complex. This may be achieved by:

- Selection of compatible materials.
- Selection of overall relative sizes of anodic and cathodic surfaces in the given environment.
- Avoidance of small anodic surfaces in conductive proximity to large cathodic surfaces within the critical part of the product's geometry.
- Specification of sound, continuous, and efficient surface coverings and coatings to be applied on both anodic and cathodic surfaces. If only one surface can be coated, this must always be the cathodic one. Adequate inspection of the continuity of surface coatings (especially on anodic metals) should be specified on products to be used in a conductive environment. (Note: Sacrificial anodes are excepted).

- Provision for formation and re-formation of continuous protective films.
- Various preservation methods make diverse demands on the shape, form, and continuity of surfaces, to attain their maximum efficiency in application techniques and their results.

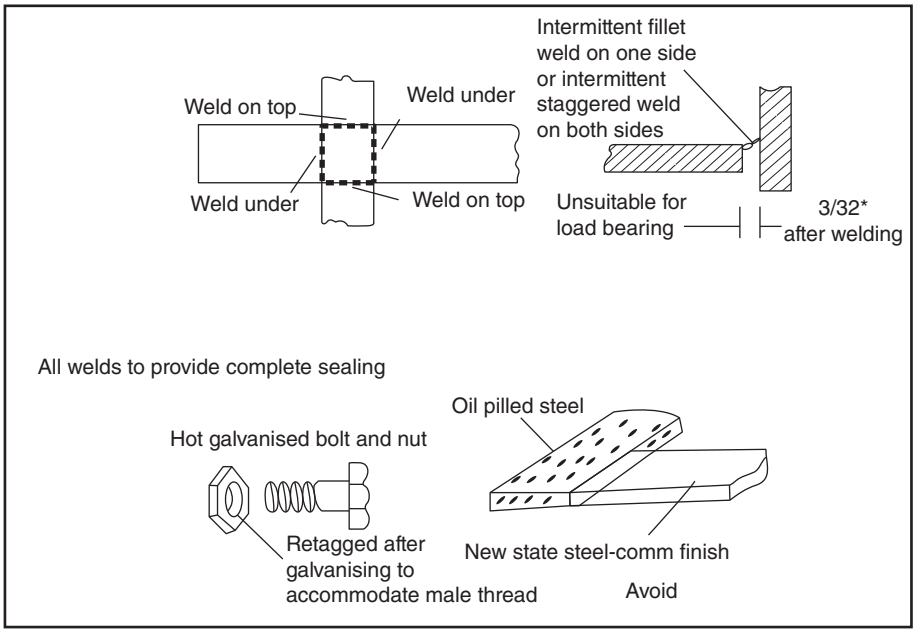


Figure 10.6 *Design for galvanizing. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

Table 10.1 *Design for plating*

Flat surfaces	Use 0.38 mm/25.4 mm in crown to hide uneven buffing undulations
Sharply angled edges	Round the edges 0.8 mm minimum radii
Flanges	Use generous radius on inside angles and taper the abutment
V-shaped grooves	Use shouldow and rounded grooves
Ribs	Use wide ribs with rounded edges. Taper each rib from the center to both sides and round off edges. Increase spacing if possible
Spear-like juts	Crown the base and round off all corners

- Select suitable surface and jointing patterns – design for painting and design for galvanizing (see Figure 10.6). Table 10.1 shows details of plating design.
- Avoid, if possible, unnecessary discontinuities in the surface flow; use continuously welded joints instead of spot-welded or riveted joints; avoid unnecessary crevices, ledges, cups, recesses, etc.
- Level out excessive roughness of surfaces – grind down any protrusions (see Figure 10.7); fill in any hollows, creases, and scratches with metal (e.g. lead, tin, etc.), plastic, or plastic metal fillers (see Figure 10.8).
- Avoid the haphazard application of insulation and surface coverings and consider the likelihood of creating adverse corrosive conditions (chemical effect, thermal, or electrochemical imbalance) or forming crevices on the surfaces of metals subject to excessive crevice corrosion damage (e.g. stainless steels); this also applies to the application of surfactants (see Figure 10.9).
- Plan precautions leading to reduction of surface damage to materials, products, and components on storage, fabrication, or erection (untreated, pretreated, or fully treated). These precautions can either apply to the product itself or to the provision of ambient conditions from outside the boundaries of the component.
- Where a surface damage by filiform corrosion on storage can be expected, provide for storage of coated metals in a low-humidity environment; coat metals with brittle film; use low-permeability permanent or temporary coatings.

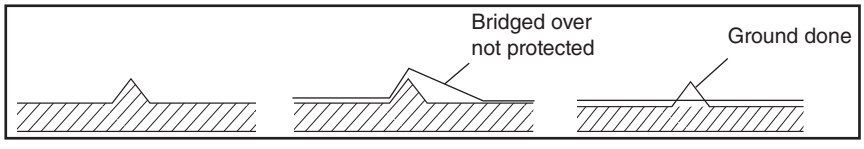


Figure 10.7 *Level out excessive roughness of surfaces.*

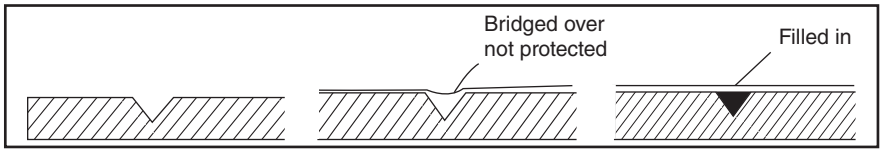


Figure 10.8 *Fill in any hollows, creases and scratches with metal. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

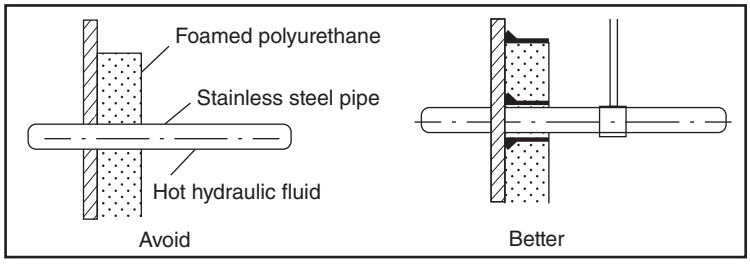


Figure 10.9 *Avoiding haphazard application of insulation and surface coverings. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

10.1.2 Structures

- Avoid adverse corrosive effects of the relative position and shape of adjoining surfaces on any of the individual strength members of the structure (see Figure 10.10).
- Introduce rounded corners in design or specify round grinding where possible. The overall design should allow easy access for grinding of corners (see Figure 10.11).
- Avoid surfaces that support deposition and retention of dust, which causes metal to corrode (see Figure 10.12).
- Where possible, change the location of strength members from surfaces exposed to heavy corrosion loading to those that are subject to less corrosive conditions (see Figure 10.13).
- Reduce the number of protruding fasteners (bolts, rivets) to a reasonable minimum. Preferred welded joints aid shaping of optimal surfaces. Monolithic components are best, if practicable (see Figure 10.14).
- Continuously welded joints facilitate optimization of surfaces, intermittent, or spot welding should not be used in strength structures, unless necessary.
- Butt-welded joints provide a better surface shape than lap joints (see Figure 10.15).
- Countersunk rivets or screws secure a better surface profile than other types of corresponding fasteners (see Figure 10.16).

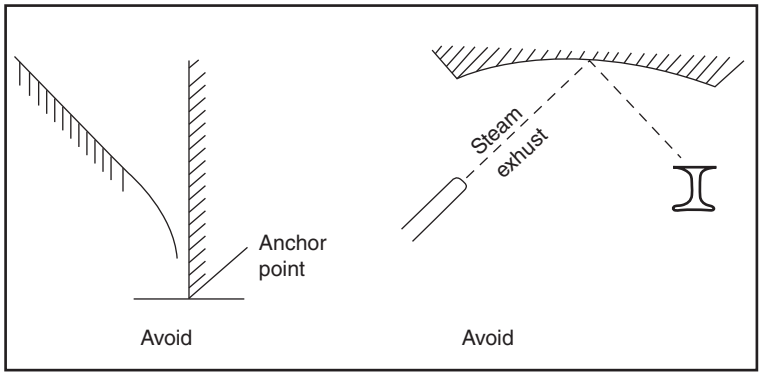


Figure 10.10 *Avoid adverse corrosive effects of the relative position and shape of adjoining surfaces on any of the individual strength members of the structure.*

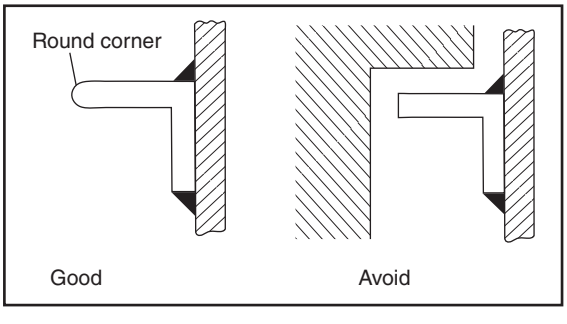


Figure 10.11 *Introduce rounded corners in design or specify round grinding where possible. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

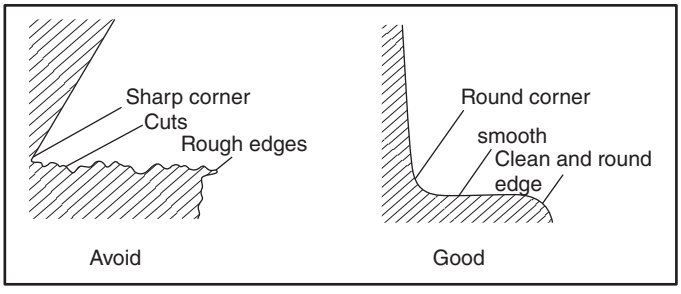


Figure 10.12 *Avoid surfaces that support deposition and retention of dust.*

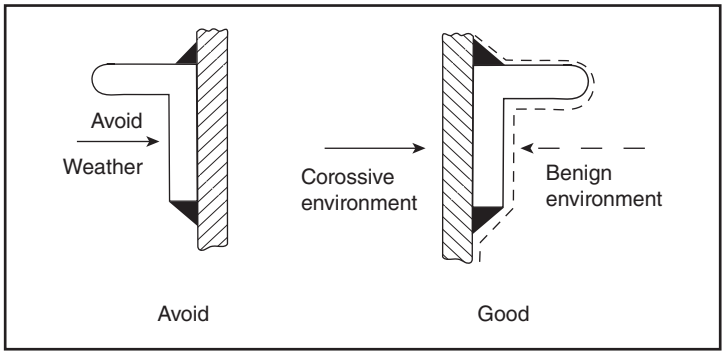


Figure 10.13 *Change the location of strength members from surfaces exposed to heavy corrosion loading to those that are subject to less corrosive conditions. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

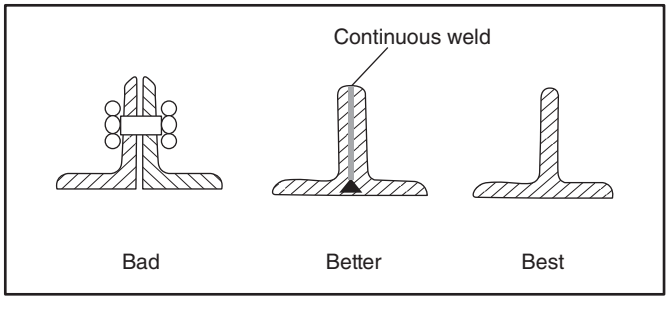


Figure 10.14 *Reduce the number of protruding fasteners (bolts, rivets) to a reasonable minimum.*

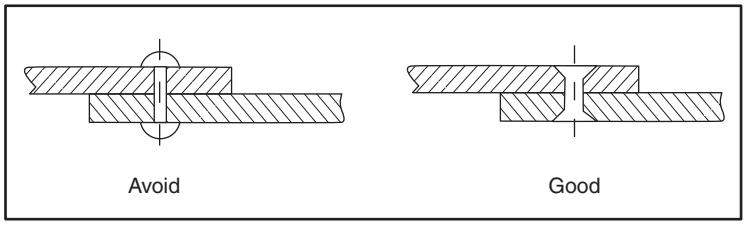


Figure 10.15 *Butt-welded joints provide better shape of surface than lap joints.*

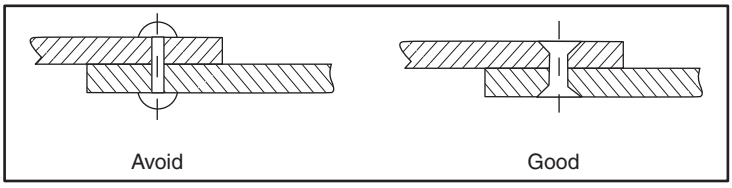


Figure 10.16 *Countersunk rivets or screws secure a better surface profile than other types of corresponding fasteners. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

- Long horizontal runs of welding should not be used in structural channels and grooves where water can lodge.
- In the design, avoid any welding in pockets thatare not accessible for cleaning, grinding, or blasting.
- Thorough finishing or smooth grinding of welds is of prime importance for securing a sound, clean surface. Specify the removal of flux, weld metal spatter, welding residue, burrs, and other similar surface defects, whenever possible, prior to any type of overall surface cleaning.
- Temporary lugs and brackets shouldould be removed and their original positions ground smooth.
- For structural steel designated for pickling, the geometry and fabrication techniques should provide homogeneous continuity of surface without crevices, ledges, cups, or recesses where the pickling liquid could penetrate and be retained.
- Crevices appearing between joined structural members prepared for galvanizing should be fully enclosed by sound, poreless, and continuous welds.
- Design welded pipe assemblies that are to be galvanized with full open mitre joints.
- In planning for reliable, long-lasting sealed joints the designer should consider the stresses that may be imposed on the sealant by the movement in joints as follows:
  - Normally, the sealant in a wider joint will be strained less than in a narrow joint during expansion, if the sealant is filled to the same depth in both joints.
  - If the joint movement amounts to 15–35% of the total joint width, a shouldow sealant depth in a wide joint will minimize stress on the sealant and on its adhesive bond to the substrate (this applies to expansion, butt, capping, and some floor, lap, and corner joints).
  - Generally, vertical joints will move more than horizontal ones, and will require shouldower sealant application.
  - If a joint exceeds standard criteria, it can be modified by the introduction of back-up material to build upon (polyethylene foam, closed cell urethane foam, or clean jute). Back-up material, before insertion, should be from 25 to 50% wider than the joint. Substrate surfaces within the

joint should be primed with an inhibited paint and the back-up material should either contain inhibitor or be dipped in inhibited paint (e.g. zinc chromate primer) prior to assembly.
  - Sealant performance is improved under stress if it adheres only to the sides of the joint and not to the bottom.

- Secure continuity of surface flow, if suitable, for extensive structural installations, by wrapping the structural members with inhibited sealing or wrapping tapes.
- Angle and shape structural surfaces to be cathodically protected for optimum efficiency, if possible.

10.1.3 Equipment

- Provide uniform surfaces on the corrosion-prone side of designed equipment.
- Reduce the number of crevices, grooves, and in-going pockets and sharp corners in the surface to a necessary minimum. If these are necessary, design for self-draining.
- In aggravated conditions, and design permitting, the complete equipment or its vital parts can be totally enclosed in watertight and airtight envelopes – possibly as self-contained units.
- Use of adhesives (e.g. structural, machinery, anaerobic adhesives, etc.) for joining individual components of an assembly can assist in the formation of smooth contours and the reduction of crevices, design permitting.
- To retain the lubricants and thus prevent corrosion, the surfaces of a piece of equipment can be roughened by shot blasting (very fine), blast peening, or application of various porous surfactants (electrodeposited porous metals, clad porous metals, anodizing, phosphatizing, ceramic deposition, or lining).
- High-polish rendered surfaces can help to reduce the danger of corrosion fatigue.
- Access of selective organic solvents to critical plastic parts should be prevented to avoid crazing or other damage to their surfaces.
- Cut surfaces of reinforced plastics should be effectively sealed to prevent access of water and other adverse environments to the reinforcing fibres.
- Folded light metal sheet equipment casings should provide the best possible continuity of surface, prior to galvanizing. All surfaces of sheeting should be degreased before folding and assembly.
- Provide openings, notches, and holes at points that will be lowest during conversion coating processes within each closed section, for its adequate draining, and so avoid inadequate rinsing between treatment stages, contamination of treatment baths by preceding stages, and the incomplete coating of flooded sections.
- To prevent poorly applied conversion or production coatings, provide a suitable method for hanging of parts on a finishing line, either by selecting a suitable shape for the part or by introducing into its design a permanent or temporary hanging device (flange, hook, ring, lug, or hole).
- Avoid completely enclosed sections for components on which conversion coatings will be applied; cleaning and coating solutions cannot completely penetrate into these, even if small holes are spotted in several places.
- A further problem inherent in painting the interior of box sections is solvent reflux; even if a paint film can be applied there, the solvent entrapped within can wash off the wet paint film during the baking cycle.
- Self-cleaning surfaces and adequate drainage should be incorporated in components to be conversion coated.
- Closed joints should be conversion coated before assembly; open joints can sometimes be conversion coated after the assembly.
- Provide in the design sufficient clearance to permit free movement between surfaces of movable parts after galvanizing. Generally, a clearance of 0.8 mm (1/32 inch) is sufficient.

- The design of parts to be electroplated or galvanized should be modified to provide adequate racking facilities.
- Small parts for barrel processing should be sturdy enough to withstand multiple impacts of barrel rotation.
- Provide for good electrical contact in the design of parts for electroplating.
- Provide small, flat parts to be barrel plated with grooves and dimples to prevent them from sticking in the plating bath.

10.1.4 Piping Systems (from a Surface Point of View)

- Both outside and inside surfaces of pipe systems should be evaluated for their surface parameters.
- Secure smooth surfaces on the interior of pipe systems; rough surfaces induce heavier precipitation of condensate, heavier and inconsistent deposition of water scale, uneven oxidation of surface, and other problems, and may lead to a heavy localized corrosion attack.
- Provide for a uniform film forming inside the pipe systems before or after assembly, to avoid creation of anodic and cathodic areas in respective conductive environments.
- Stabilize exterior surface conditions of insulated pipe systems.
- Secure uniformity of metal composition for surfaces in critical areas (see Figure 10.17).
- Preferably locate stiffeners on the outside of vessels containing corrosive liquids (see Figure 10.18).
- Assist in formation and upkeep of protective films in conductive media on metals that depend on such films for their protection, by an adequate and continuous supply of free oxygen.
- Secure continuity of surface flow on extensive pipeline installations, by wrapping the pipes with inhibited sealing or wrapping tapes.
- To avoid unnecessary discontinuities of interior surfaces in pipe systems, strike the right balance between the optimal reduction of joints and the optimal requirement of sections for fabrication, assembly, and replacement.
- Tube assemblies and sealed cavities (e.g. tanks) require adequate venting and drainage holes for galvanizing.

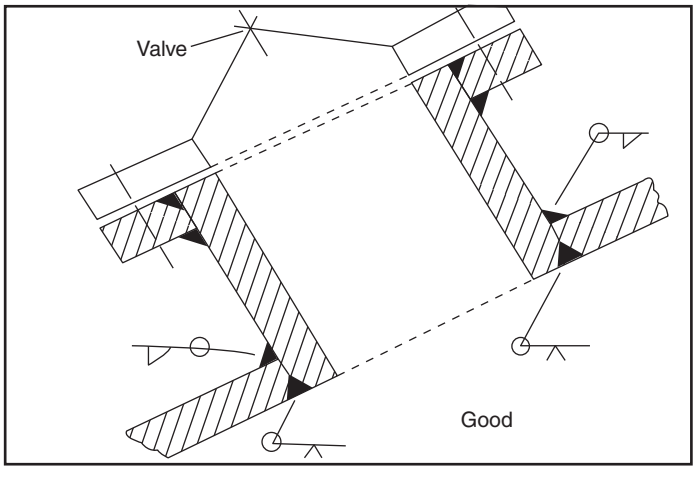


Figure 10.17 *Secure uniformity of metal composition on surfaces in critical areas.*

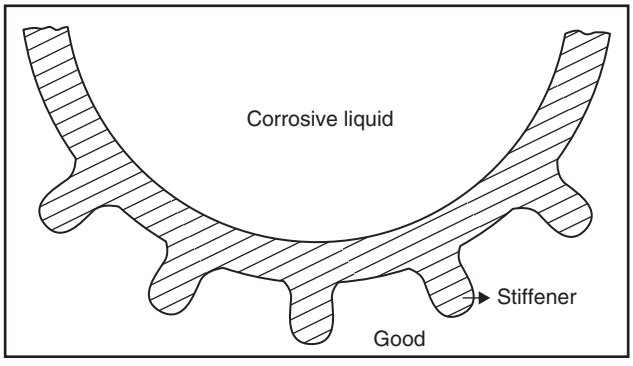


Figure 10.18 *Preferably locate stiffeners on the outside of vessels containing corrosive liquids. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

10.1.5 Surface Preparation

- Surfaces exposed to corrosive conditions should be protected at all stages of storage, fabrication, assembly, and operation – temporary or permanent protective measures can be used.
- The texture of surfaces (surface finish) has considerable influence not only on the mechanical performance of the component, reduction of friction and control of wear but also on the extension of its economic life obtained through the efficiency of the relevant corrosion-control precautions. This applies whether the materials remain uncoated or any further finish be applied.
- The principal parameters in securing proper surface finish control are as follows:
  - Machining or application cost control
  - Friction reduction
  - Wear control
  - Lubrication control
  - Durability
  - Holding of tolerances
  - Precise fittings
  - Resistance to initiation of corrosion
  - Economic permanency of corrosion control
  - Application of protective coatings
  - Final appearance
  - Consistency of operation
  - Reduction of vibration.
- Where a film of lubricant must be maintained between two moving parts (bearings, journals, cylinder bores, piston pins, bushings, pad bearings, helical and worm gears, seal surfaces, machine ways, etc.), the surface irregularities must be small enough to avoid penetrating the oil film under the most severe operating conditions but not so small as bring loss of lubricity in cases where boundary lubrication exists or where surfaces are not compatible (e.g. surfaces are too hard).
- Smoothness and lack of waviness are essential on high-precision pieces for accuracy and pressure-retaining ability (injectors, high-pressure cylinders, micrometer anvils, gages, and gage blocks).
- Smooth surfaces bring elimination of sharp irregularities, which are the greatest potential source of fatigue cracks on highly stressed members subjected to load reversals.
- Smoothness of final appearance can also be controlled by production tools (rolls, extrusion dies, precision casting dies).

- Surface finish control of such parts as gears may be necessary to secure quiet operation and to reduce vibration.
- The surface finish should be a compromise between sufficient roughness for proper wear-in and sufficient smoothness for expected service life.
- Incorrect clearances between two surfaces in relative motion may result in local hot spots and high oil consumption.
- Excessively rough textured surfaces increase turbulence, retain more dust, and lead to heavier precipitation, retention of condensate, and deposition of water scale – all detrimental to proper corrosion control.
- Specify, where possible, for grinding of excessively rough surfaces to a smooth contour.
- Evaluate, in each individual case, which texture of surface gives the best anti-corrosion service and specify this degree of surface roughness in the design. Observe that it is not always sufficient to specify only the texture of the substrate, but that the texture and consistency of preservation coatings or surfacing materials may also be required.
- In the interests of corrosion control the designer should consider, at the design stage, whether the components should remain as supplied, untreated as machined, or whether they should be ground, honed, polished, flash rusted, blast cleaned, blast peened, roughened, anodized, passivated, metallized, surfaced, sealed, prefabrication treated, or painted.
- The maximum acceptable surface roughness compatible with the service and fabrication requirements should be specified preparatory to the application of protective coatings. Very smooth surfaces (e.g. new hot dip galvanizing, polished components, etc.), on the other hand, may require flash rusting, etching, phosphatizing, anodizing, or abrasive blasting at various stages of fabrication or assembly to give optimum adhesion conditions.
- Surfaces roughened by very fine shot blasting or by application of porous coatings (electrodeposited porous metals, ceramics, anodizing, or phosphatizing) can better retain lubricants and thus help to prevent corrosion.
- Surface conditions in design should be reconciled with the surface treatments to follow and their requisite application techniques – surfaces and their treatments are complementary to each other.
- All materials must be cleaned. Select and specify in the design the mandatory method and standards in detail. Cleaning methods and techniques that render the best economic results within the whole life-cycle of the utility are preferred.
- Unless the specified cleaning operations on their own can automatically provide for the following, the removal of burrs, notches, flares, fluxes, weld metal spatter, etc., should precede the specified surface cleaning.
- Specify complete removal of mill scale on steel – partial removal is a waste of money.
- Select the economically advantageous removal of rust, considering the merit of long-term economy.
- Specify removal of oil, grease, finger marks, salt deposits, and various organic and inorganic contaminants from the surface before and/or after the programmed physical and chemical cleaning to suit the purpose.
- Cathodic cleaning of high-strength steels in either acid or alkaline baths should be avoided, anodic cleaning is permissible.
- Flame cleaning should not be specified for removal of mill scale in a new unbroken state from steel.
- Blast cleaning is preferred to pickling for hot rolled parts with machined surfaces.
- All assemblies of cast iron, cast steel, and malleable iron with rolled steel should be blast cleaned after assembly and prior to pickling (different pickling characteristics).

- Dissimilar materials (different analysis steels or different surface finishes of steel in an assembly) should be pickled and galvanized separately and assembled after galvanizing for uniformity of surface appearance.
- Corrosion control prefers, in general, the surface cleaning methods given in Table 10.2.
- Avoid specifying excessive roughness of surface for application of protective coatings (See Figure 10.19)
- The specified blasting profile (amplitude and shape) should be adjusted to the thickness consistency, external smoothness, and adhesion of the coating that is to follow (Table 10.3).
- Surface hardening and hard surfacing of metals should be evaluated for a possible substantial aggravation of corrosion.
- Specify, if required, suitable surfacing materials (metals, ceramics, mastics, deck covering underlays, cements, fillers, noise damping and anti-condensation compounds, plastic and reinforced

Table 10.2 *Surface cleaning methods*

Material	Preferred surface-cleaning method
Steel	Abrasive blasting
Aluminum	Abrasive blasting – very fine grade abrasive
Copper	Mechanical cleaning, followed by wash with solution of 5% zinc chloride and 5% zinc muriatic acid at commercial concentration in water
Nickel	Abrasive blasting – non-metal abrasive
Stainless Steel	Abrasive blasting – non-metal abrasive
Zinc	Mechanical cleaning followed by wash with phosphoric acid solution, followed by removal of zinc salts

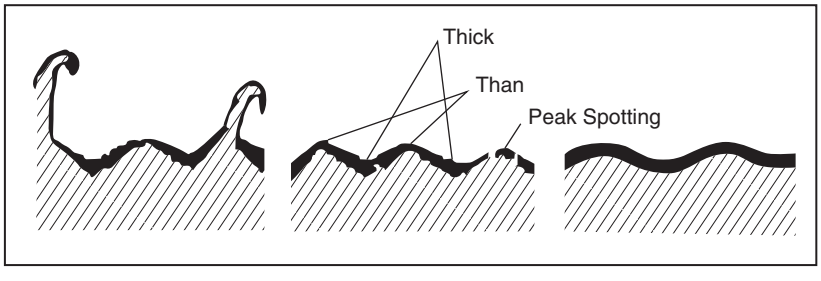


Figure 10.19 *Avoid specifying excessive roughness of surface for application of protective coatings. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

Table 10.3 *Recommended maximum profile amplitudes (normal conditions)*

Application	Amplitude	
	mil	μm
Prefabrication primer	2	51
Standard paints	3–4	76–102
High build paints	5	127
Sprayed metals	5–8	127–203
Electrodeposited metals	2	51
Removal of foreign matter (close tolerance surface)	Nil	Nil

plastic linings and surfaces, potting compounds, rubber linings and metal-filled surfaces) for protection of relevant surfaces (e.g. against cavitation on propellers, cylinder liners, pumps, impellers, etc.) and for build-up of surfaces to a uniform level, optimum surface profile (e.g. for drain ability, improvement of contour and fairing and for improvement of appearance), or for fill-in of spaces that cannot be otherwise preserved. The degree of surface roughness of surfactants should also be indicated.

- Prefabrication treatment of steel should provide for adequate protection on storage, fabrication and assembly, until such time as the final coatings can be applied (approximately 6–9 months).
- Pipe purchased for fabrication and galvanizing should be ordered without mill scale or the mill scale should be removed by blast cleaning prior to pickling.
- Pipe fittings for galvanizing should be of uncoated steel.
- Markings and lettering applied to surfaces to be galvanized should be made in water-soluble colors or otherwise be punched.

10.1.6 Electrical and Electronic Equipment

- Specify and design for smooth surfaces without crevices, as far as practical.
- Joints should be continuous and impervious.
- Crevices, especially those in stainless steel (i.e. joints, under washers, etc.), should be sealed with suitable sealants (e.g. polysulfide, polyurethane, rubber) or petroleum jelly.
- Non-hydroscopic insulation should be used.
- Marker tapes should be specified for use only on surfaces that have been treated previously.
- Proper, thorough, and compatible cleaning methods should be specified before joining, coating, potting, impregnation and encapsulation of components.
- Flux residues should be removed after brazing and soldering.
- Welds should be cleaned, after welding, of scale, fluxes, spatter, oxidation, and rough areas.
- Fingermarks should either be prevented or removed.
- Surface contaminants should be removed from conductor surfaces by an appropriate cleaning method. This shold be followed by priming with a de-ionized organic moisture barrier for protection.
- No aggressive cleaning methods should be used on printed circuit boards.
- The use of solid metals or plating with such metals as gold, rhodium, and platinum, which are inherently resistant to tarnishing, should be specified to ensure maintenance of maximum conductivity.
- Electromagnetic compatibility of electrically bonded metals should be secured by the selected surface finish (see Table 10.4).
- Avoid using exposed soft solder at joints prior to electroplating.
- Resistance welded joints should be sealed.

10.2 Protection

The function of protection is, to a considerable degree, the upkeep of the optimum anti-corrosion factor built into the particular design itself. Protection on its own, therefore, cannot normally take sole responsibility for preservation of a utility in a usable state. Both the intrinsic corrosion-control provisions and properties that are kept captive within the material boundaries of the designed structure or equipment, and the corrosion-protection activities that are applied from without, are complementary

Table 10.4 *Electromagnetic compatibility of electrically bonded metals secured by the selected surface finish*

Metal	Surface finish
Aluminum 1100, 3003, and clad alloys	Bare of chromate-type film treatment Low electrical resistance Tin lead (solder) plate or tinplate preferred
Aluminum (all other alloys)	Cadmium plate chromate-type chemical film treatment Low electrical resistance
Copper, copper alloys	Bare, tinplate or tin lead (solder) plate preferred Cadmium or gold plate
Cadmium	Bare or chromate-treated
Iron and steel	Tinplate or tin lead (solder) plate preferred Cadmium plate
Magnesium	Bare; clean immediately before and coat joint immediately after bonding
Nickel and corrosion-resistant steels	Bare; difficult to bond because of adherent oxide film
Silver	Bare
Solder	Bare
Tin	Bare

to each other. The demarcation of their respective boundaries will be largely governed by the rational trade-off of their comparative economic values.

High costing protection may favorably balance the appropriate replacement of more exotic materials or geometric forms with cheaper ones; it may favourably compensate for reduction in strength, for less frequent maintenance, for better safety of operations, etc. Use of cheap protective measures may often prove false economy.

Protection should be tailored to the particular assembly complex and not to the individual composite parts, subassemblies, or units. For optimum protection, consideration should be given to the geometry and location of the utility and its vital parts, ease of application and the effectiveness of the protective measures, these factors being reciprocally adjusted to suit each other. New or revolutionary protective measures and techniques should not be incorporated haphazardly in design – structures and equipment should be designed for their most effective use. The more inaccessible the surfaces, the better should be their protection. Active or passive ecological involvement of protective measures is of prime importance.

Only necessary, safe, and economically feasible protection should be specified, preferably by methods and techniques applied under controlled or automated conditions, thus eliminating or reducing the adverse influence of human variance. The local obtain ability of an efficient and expert labor force, as well as local climatic conditions at the initial production site and at the subsequent ports of call, will have a considerable influence on the selection of protective measures. Where these factors can have a critical effect on the efficiency of protection, preference should be given to those materials, methods, and techniques that can give the best results when used at the specific locality.

Basically, protection comprises those measures providing separation of surfaces from the environment, those giving cathodic protection or anodic polarization, and those that cater for adjustment of environment. These methods can be used individually or in various combinations, the latter affording a greater degree of protection that the sum of individual effects.

To decide on required and economically feasible protection the personnel engaged in this task have a vast variety of protective measures, systems, methods, techniques, and especially competitive products to choose from. Extensive engineering investigation, independent suitability testing, and practical proof of effectiveness may be needed to precede the final choice.

The designer should seek enlightenment on specialties from dedicated and, if possible, independent specialists – in fact, co-operation is a necessity for a designer engaged in creative design. The designer, who is not a corrosion specialist, cannot acquire an encyclopedic knowledge of all relevant disciplines.

For these reasons, and to allow the designer the intelligent insight necessary for the formulation of the design policy, only an outline of procedures is recorded in this book, the details being left to the correctly reasoned effort of all interested parties co-operating in the design team and the specialized information at hand.

10.2.1 Requirements

Separation of materials from the environment, provided by the following applications:

- Cladding
- Painting
- Lining with organic and inorganic materials
- Coating by non-metallics
- Application of metallic coating
- Thermal insulation and isolation
- Electrochemical cathodic and anodic protection
- Protection by adjustment of environment.

All the above applications involve primarily a change in surface composition, caused by the addition of different materials (metallic or non-metallic) in the form of an outer skin. Most of these processes involve a dimensional change (except perhaps diffusion coating) and also a weight change.

10.2.2 Protection by Separation of Materials from the Environment

- Ideal separation of the surface requires total exclusion of air and moisture or other corrosive media from the protected surfaces. This is difficult to achieve due to the inherent porosity of various protective materials, the limited survival life of these materials, and the tendency of these materials to application faults.
- To provide against any deficiency in effective separation of surfaces, recourse is normally made to multi-phase combinations of separation materials applied to surfaces in a form of protective systems, which combine several materials, either of the same family or of several complementary categories.

10.2.2.1 Selection of Protection System

Make the basic decision as to the type of separation method to be used with respect to the following considerations:

- Which single or combined method can provide the optimum period of respite from repetitive maintenance and preserve the operational function and anti-corrosion integrity in the given environment?
- Which methods are compatible with the materials to be preserved and, if a combination of separation methods is considered, whether the whole system will be compatible throughout?

- Which methods will suit the considered geometric form initially and at repetitive maintenance; which method will suit the requirements of frictional joints?
- What will be the effect of thermal shock, abrasion, impact, overheating, and cryogenic temperatures on the selected system?
- What stage of fabrication and assembly may be critical for the optimum application of considered methods to fit well into the production program?

10.2.2.2 Metal Coating

Metal coating processes can be classified as anodic or cathodic. The anodic ones will protect substrate metal (even when porous or damaged) through their preferential corrosion, whereas the noble metal coatings, which are mainly used for their superior chemical-resistance properties, will accelerate the corrosion of the metallic substrate in such circumstances (see Table 10.5).

It is necessary to protect anodic coatings (particularly the porous ones) with sealers or paints, especially when exposed to acids, marine environments, or other corrosive conditions.

Make the basic decision on the optimum coating metal and its method of application:

- Decide which coating metal will withstand the expected environment; and which of the coating metals can be applied to adequate thickness with good coverage. Note: The danger of microcracking of thickly applied chromium, rhodium, or hard metals; (corrosion rate of deposited metal from economical and technical point of view).
- Which combination of metallic coating and substrate can provide optimum porosity and galvanic relationship?
- Consider if the coating method change the physical properties of the substrate.
- Will the coating metal allow the desired physical properties (appearance, color, brightness hardness, strength, wear resistance, temperature resistance, electrical conductivity) at the required cost and is the optimum technology readily available?

In the case of electrode position, consider the following:

- Which desirable physical, mechanical, and chemical properties, and what composition of deposited metal are required?
- What thickness of coating is required? (Note: the nature of substrate, nature of coating, environmental conditions, and economics.)
- What hardness of deposits is required?
- What precautions are necessary to reduce input of high tensile stresses in the deposits?
- What precoating is required to secure effectiveness of deposits?
- Will the substrate be adversely affected by the process solutions (e.g. hydrogen embrittlement)?
- Which available method of application is suitable for the designed component (vat process, barrel process, brush plating, chemical reduction, etc.)?
- What are the desired main and side effects of deposition (corrosion protection, decorative, specular and heat-reflective finishing, wear resistance, prevention of galling, stopping-off during carburizing, electroforming, etc.), and which particular technique can provide the optimal results?
- Which of the practical applications is most suitable for the composite of materials, geometry, surfaces, and size of the component?
- What effect will the environmental conditions have on the deposited coatings and, if subject to abrasion, what will be the edge effect of deposited metal on the substrate?

Table 10.5 *Typical list of metal coatings on steel*

Process	Coating	Potential	Dry film thickness (mil; μm)	Use or limitation
Aluminizing	Aluminum	Anodic	1–6; 25–152	Factory process
Brush plating	19 metals	Various	0.01–6; 0.25–152	Waveguides, site work
Cathode sputtering	Metals, ceramics	Various	4; 4	Special applications
	Cobalt	Noble/cathodic		
Chemical reduction	Copper	Noble/cathodic		Special applications
	Nickel	Noble/cathodic	0.1–1; 2.5–25	Printed circuit boards
	Palladium	Noble/cathodic		Special applications
	Metal alloys	Various		
Detonation spray	Metals, ceramics	Various	1–12; 25–305	Best quality Special applications Hard surfacing
Diffusion coating	Metals, silicates	Various	0.01–30; 0.25–760	Special applications
	Aluminum	Anodic		
Electrophoresis coating	Molybdenum	Noble/cathodic	1–10; 25.4–255	Small parts
	Nickel	Noble/cathodic		
	Aluminum	Anodic	0.25; 6.5	
	Cadmium	Anodic	0.15–0.5; 4–12.5	
	Chromium	Noble/cathodic	0.005–20; 0.15–510	
	Copper	Noble/cathodic	0.01–30; 0.25–760	
	Brass	Noble/cathodic	0.07–0.1; 1.8–2.5	
	Gold	Noble/cathodic	0.03–0.8; 0.75–20	
	Silver	Noble/cathodic	0.1–1; 2.5–25	
Electroplating	Iron	Various	> 125; > 3175	Wire, sheet, small parts
	Lead	Noble/cathodic	0.25–50; 6.5–1250	
	Nickel	Noble/cathodic	0.1–2.2; 2.5–55	
	Platinum	Noble/cathodic	0.1–1; 2.5–25	
	Palladium	Noble/cathodic	0.1–0.2; 2.5–5	
	Rhodium	Noble/cathodic	0.01–0.02; 0.25–0.5	
	Tin	Noble/cathodic	0.2–2; 5–50	
	Zinc	Anodic	0.1–1; 2.5–25	
Explosion bonding	Metals	Various	60–750; 1525–19050	Plates, tube sheets, strip
	Aluminum	Anodic	4–8; 100–205	Porous, needs sealing
	Zinc	Anodic	2–5; 50–125	Porous, needs sealing
Flame spraying	Tin	Noble/cathodic	3–15; 75–380	
	Metals Ceramics	Various	5–60; 125–1525	Low-melting alloys
Fusion bonding	Metals	Various	60–750; 1525–19050	Plates, tubes
Galvanizing	Zinc	Anodic	0.5–5; 12.5–125	Maximum length 24 m (80 ft)
Gas plating	Metals	Various	0.01–70; 0.25–1780	Special applications

Table 10.5 *(continued)*

Process	Coating	Potential	Dry film thickness (mil; μm)	Use or limitation
	Copper	Noble/cathodic	0.05; 1.25	Special applications
	Silver	Noble/cathodic		
Immersion plating	Tin	Noble/cathodic		
	Lead	Noble/cathodic		
Ion plating	Metals	Various	Thin film	Special applications
Lead coating	Lead	Noble/cathodic	0.185; 4.7	Special applications
	Aluminum	Anodic	10–300; 250–760	Sheets, plates, strips, tubes
	Brass	Noble/cathodic	60–750; 1525–19050	Transition joints
	Copper	Noble/cathodic	60–750; 1525–19050	Special applications
	Lead	Noble/cathodic		
	Magnesium	Anodic		
Metal cladding	Nickel alloy	Noble/cathodic	60–750; 1525–19050	
	Palladium	Noble/cathodic		
	Platinum	Noble/cathodic		
	Silver	Noble/cathodic		
	Stainless steel	Noble/cathodic	5–750; 127–19050	
	Tin	Noble/cathodic		
	Titanium	Noble/cathodic	31–400; 790–10160	
	Tantalum	Noble/cathodic	20–125; 510–3175	
Ox hydrogen spray	Ni-Cr-Al	Noble/cathodic	0.5–1; 12.5–25	Special applications
Peen plating	Aluminum	Anodic	2; 50	
	Cadmium	Anodic		Special applications
	Lead	Noble/cathodic		
	Tin	Noble/cathodic		
	Zinc	Anodic		
Plasma spraying	Metals, ceramics	Various	0.01–100; 0.25–2540	Better quality high-temperature melting metals
Sherardizing	Zinc	Anodic	1–3; 25–75	Small parts
Swab plating	Metals	Various	0.01–6; 0.25–150	Special applications
Terne plate	Lead/tin	Noble/cathodic	0.01–1; 0.25–25	Sheet steel
Tin dipping	Tin	Noble/cathodic	0.006–1.2; 0.15–30	Special applications
Vacuum deposition	Metals, ceramics	–	0.01–3; 0.25–75	Special applications
	Aluminum	Anodic	0.5–1; 12.5–25	Special applications
	Chromium	Noble/cathodic	0.1–1; 2.5–25	
Vapor deposition	Iron	–		
	Nickel	Noble/cathodic	1–100; 25–2540	
	Graphite	Noble/cathodic		
Mechanical plating	Cadmium	Anodic		Special applications
	Tin	Noble/cathodic		
	Zinc	Anodic		
Hard facing	Metals	Various	30–400; 760–10160	Special applications

- Which will be the best way to secure non-porosity and uniformity of cathodic/noble coatings?
- Which method of sealing will be compatible with the anodic metal deposits?

In the case of hot-dip metal deposition, consider the following:

- Will the composite of materials, geometry, surfaces, and size of the components suit the available practical application?
- Will the basic metal be adversely affected by the pretreatment process solutions?
- What effect will the environmental conditions have on the deposited metal coating and, if subject to abrasion, what will be the edge effect of deposited metal on the substrate?
- What thickness or weight of coating is required to provide the optimum protection?
- Will the reduction of coating thickness (by rolling, wiping, centrifuging, etc.) of molten metal be required to secure the relevant thickness?
- Will the improvement of properties or appearance of coating by chromatizing, phosphatizing, light rolling or roller levelling be required, and will the removal of palm oil or other post-metallizing treatment be necessary on production?
- Will any change of character of the coating by annealing and conversion, by anodizing or dyeing, be required?
- Will painting of the deposited metal be required?
- Will any preparation or pretreatment of the deposited metal be required prior to further coating?
- Will any joining be possible after metal deposition; which techniques can be used where hot-dip coatings are applied to raw materials prior to fabrication?

Typical detailed appreciation of hot metal spraying (corrosion prevention; sprayed lead for use in atmospheres containing sulfuric acid; tin for food vessels; stabilized stainless steel, nickel and Monel for pump rods, impellers, etc., for build-up; hard facing; spray welding; etc.):

- What will be the purpose and use of the metal-sprayed coating?
- Which system of metal spraying will offer the optimum results (molten metal, metal powder, metal wire, electric arc, detonation spray, plasma spray, or other)?
- Will the bond strength of the flame-spray applied coating exceed the design stress at the interface?
- Will the surface roughness of the substrate be comparable with the particle size of the sprayed metal?
- Will the composite of materials, geometry, surfaces, and size of the components suit the available practical application?
- What effect will the environmental conditions have on the deposited metal coating and, if subject to abrasion, what will be the edge effect of the deposited metal on the substrate?
- What thickness of coating is optimal and can be applied to the substrate without obvious shear stress between dissimilar metals (shrinkage), which may arise, especially in environmental conditions of fluctuating temperature, sustained vibration, etc.?
- Will overall uniformity of thickness and minimum porosity be obtained?
- What hardness of the coating is required?
- What sealing will be necessary to counteract the porosity of the sprayed metals?

For critical applications, and since thermal-sprayed coatings are not homogeneous materials, it is further advisable to consider:

- Behavior of melted particles on passage through the flame and the change in composition involved, pick-up of contaminants, embrittlement of layers and its influence on thermal expansion, thermal conductivity and strength of the coating.

- Some metals show higher strength on the plane parallel to the surface than the one perpendicular to it.
- Porosity influences the strength of ductile and brittle coatings, and therefore the pore size, shape, and volume of porosity should be evaluated.
- Porosity is influenced by variables such as torch to substrate distance, spray environment, substrate temperature, and spray process.
- Pore volume decreases the heat conductivity of the coating.
- The bond strength must exceed the design stress at the interface and this is relative to the true surface area, its roughness, and the thickness of the coating.

In the case of diffusion coatings, consider the following:

- Will the composite of materials, geometry, surfaces, and size of components suit the available practical application?
- Will the basic metal be adversely affected by the pretreatment process solutions and by the heat of compression of the diffusion process?
- What effect will the environmental conditions have on the diffusion layer and what will be the edge effect when damage occurs?
- Will the process secure the overall non-porosity of the coating?
- Will normalizing, air-hardening, and other pretreatments, air or gas welding, brazing and silver soldering, etc. adversely affect the diffusion coating?

10.2.2.3 Coating System (Paints)

The complete coating system is a complex multi-purpose finish, performing protective, sealing, and decorative functions (it may also provide lubrication, conductivity, etc.). The system is the basic engineering unit of surface separation rendered wholly or partially by surface coatings or linings. The complete system comprises:

- Preparation of surface to provide optimum interface.
- Application of the required film thickness of the anti-corrosive medium (metallic or non-metallic), the thickness depending upon the service requirements of the coating system.
- Application of the required thickness of sealing and/or decorative medium (sealer) to secure sufficient impermeability against the environment and thus to extend the functional readiness of the anti-corrosive medium.
- Application of special-purpose coatings (anti-condensation, noise damping, etc.).

The most important parts of the coating system are the preparation of the surface and the selection and application of the anti-corrosive medium (various anodic metallic coatings, prefabrication primers, organic or inorganic corrosion-inhibiting primers, conversion coatings, anodizing). Undercoats are only for improvement of appearance.

Prefabrication primers are an important part of the whole preservation system. Their integrity should therefore be preserved throughout the process of manufacture, and every economically sound remedial action taken to repair any damage as soon as possible whilst fabrication proceeds, and definitely prior to the application of the next coating; one area should remain untreated and open to corrosion for extended periods. All necessary activities should be included in the production planning.

Prefabrication primers should satisfy the following requirements:

- Cover adequately the contours of the surface.
- Allow easy application by brush, roller, spray (all types including electrostatic spray), or by any other method available, required, or suitable.

- Secure a fast drying time – not more than 5 min for spray application and 20–30 min for brush or roller applications.
- Have a reasonable pot life.
- Supply good temporary protection by a thin film both before and after fabrication, until such time as the full paint system can be applied.
- Provide good, if possible permanent, base for the widest range of subsequently applied coatings.
- Be free of toxic fumes on cutting and welding.
- Will not interfere adversely with flame cutting and welding operations, or the quality of the weld outside of established parameters – will also provide only for a minimum back burn without major damage.
- Will withstand cold working of the metal without flaking.
- Be electrically conductive where earthing in fabricated structure is required.
- Possess good resistance to abrasion and good adhesion to withstand fabrication, transportation, and erection.
- Be reliable when used under cathodic protection.
- Be eventually tintable in various colors for marking different grades of basic construction steel, for marking distinctive sections of structures, etc.

There is a large range of primers to choose from, differing in their purpose and quality. The differences, however, are not confined to the variety of utility and quality within each generic group, but also apply to the design of the coating regarding its method of application and the thickness of the applied film.

Where the coating is to be applied to a relatively smooth surface, with no sharp peaks and for a limited or temporal utility, then a thin film (e.g. prefabrication primer only, etc.) may suffice. Where the texture of the surface is rather more pronounced, where the corrosive conditions are more aggressive, and where extended protection is needed, then a thicker film is required; in this case the original pretreatment should be extended by addition of one or more further coatings of primer to suit. Two-step application procedures should be used.

Where the texture is even coarser, as on corroded steel, a very thick film is required. In this case, high build primers can be used, the number of coats varying with the expected life and environmental conditions.

A sealer primarily means any coating or lining that is applied on top of anti-corrosive compositions for the purpose of extending their utility in an efficient state for an economic period. The general requirements of a good sealer are as follows:

- Good adhesion to the anti-corrosive composition
- Low permeability to water or other corrosive media
- High film thickness
- Good chemical resistance
- Optimal resistance to abrasion
- Good weather resistance, including resistance to ultraviolet light.

Where protection is required against atmospheric corrosion only (e.g. under rural conditions), it may not be necessary to use sealer, provided an adequate film thickness of sacrificial metal contained, for example, in a metallic or inorganic zinc coating, is applied. Otherwise an application of sealer is a necessity, observing that it is in the interests of the proprietor of a utility to avoid repetition of expensive overall preparation of surface. Sealer extends the effectiveness of anti-corrosive composition and the anti-corrosive composition prevents the onset of corrosion that penetrates through damaged and porous sealer. Both are complementary to each other.

Seventy-five percent of the success of protection depends on adequate surface preparation and reliable application. The use of technically skilled industrial and approved applicators is recommended. Engineering planning, accurate specification, and complete scheduling of protection by coatings is a necessity.

Protective coatings should only be used if it is more economical than use of corrosion-resistant metals and other materials.

Care should be taken to ensure that all materials are stored, handled, and maintained to avoid physical damage, contamination, and deterioration of the protective coatings, and the requisite precautions should be planned.

Protection by separation of surface from environment by protective coating should be evaluated together with relevant parts of "compatibility," "mechanics," and "surface." Further the problems and limitations of the applicator, climatic and working conditions, properties of materials in relation to procedures and schedules should be reviewed; application methods to suit the geometry chosen; systems that permit maximum application of money-saving practices, use of the minimum number of different materials and least number of colors selected; maintenance practice anticipated.

A typical detailed appreciation of proprietary prefabrication primers is as follows:

- Will there be suitable and effective facilities for prefabrication priming available; can the prefabrication-primed metal be supplied ex-stock?
- Will the substrate metal be suitable for prefabrication priming (type and thickness)?
- Will the handling, storing, and fabrication facilities and program be attuned to the proprietary prefabrication primer?
- What is the workmen's (trade union's) attitude towards the working of prefabrication primed metals, especially welding?
- Will the removal of primer prior to flame cutting or welding be necessary (critically loaded structures), or can arrangements be made to mask the critical welding surfaces prior to priming?
- Will it be necessary to remove the proprietary primer overall or partially prior to further coating?
- What will be the effect of weathering (in stock and in work) on prefabrication primed metal and what precautions will be necessary prior to application of further coatings?

Suitably precoated metals (fabrication process) are preferred to complete or partial postfabrication treatment, where the degree of required protection, the construction, and the joining will permit.

A typical detailed appreciation of plastic coatings is as follows:

- Will the plastic coating lend itself to application by available facilities?
- Will the process be rapid and economic enough?
- Will the plastic coating withstand atmospheric weathering conditions?
- Will the plastic coating be tough enough to endure the abrasion and impact of handling, loading, and unloading of storage and transport facilities, and stringing equipment?
- Will the plastic coating have sufficient flexibility to withstand the maximum bends utilized at temperatures from −6.7°C to 60 °C (20 °F to 140 °F)?
- Will it melt or burn back within 1.2 cm ($\frac{1}{2}$inch) of the weld and be compatible with a joint system subsequently applied to protect the weld area?
- Will it resist the impact of rocks and soil during backfill operation; also, will it resist the wear and tear of fitting and normal operation?
- Will it crack or disband during hydrostatic and other testing?
- Will it soften at temperatures below 93 °C (200 °F) when used on hot line service?
- Will it resist penetration of subsurface waters or liquid contents?
- Will it resist chemical attack from outside (e.g. natural soil chemicals, fertilizers) or inside?

- Will it be attacked by bacteria and fungus in the soil?
- Will it resist the solvent action of products in permanent contact or occasional contact in the event of overflow, spillage, or breakage (e.g. aviation gasoline, jet fuel, crude oil, etc.)?
- Will it possess the adhesive forces and chemical inertness to resist, within an economical lifetime, the effects of cathodic protection systems in soils or seawater of low resistivity?

10.2.3 Electrochemical Cathodic and Anodic Protection

The designer should decide initially whether the polarization of materials in conductive media will be secured by:

- Cathodic protection – ships' hulls and appendages, cargo and ballast compartments, bilges, sea inlets and discharges, off-shore structures, jetties and navigational aids, off-shore pipelines, harbor structures, heat exchangers, box coolers, large seawater storage tanks, buried pipelines, well casings and gathering lines, public utilities, lines and cables, buried feet of overhead power pylons and metallic telephone posts, industrial storage tanks, gas holders, bottle washing machines and other industrial plant, reinforcing rods and wires in prestressed concrete and other structures, or equipment immersed in aqueous solutions of electrolyte (pure water, river water, potable water, seawater, wet soils, and weak acids) and in weak-to-medium corrosive environments, where proportionally higher consumption of protective currents is allowed.
- Anodic polarization of active/passive metals – alloys of nickel, iron, chromium, titanium, and stainless steel in weak-to-extremely corrosive environments, where economy in consumption of protective currents is required.
- Coating with anodic metals (zinc, aluminum, cadmium), which may be appreciated either as part of surface separation or part of cathodic protection.

When the initial decision to use cathodic protection has been made, it must be decided upon whether to use impressed currents or sacrificial anodes by:

- Size and geometry of the project (impressed currents method is usually used for large projects)
- Availability of the power supply
- Possibility of interface problems
- Necessity for safety from spark hazards and accumulation of hydrogen in enclosed spaces
- Replaceability of sacrificial anodes
- Expected economic life of the system.

A typical basic appreciation of cathodic protection by sacrificial anodes is as follows:

- Estimate of total current requirements (current densities allowed, spare capacity, allowance for protective coatings and linings, assessment of environmental media)
- Resistivity of water, soil, or other electrolyte solution
- Requirements for insulating flanges and bonding to foreign structures, and assessment of extra current allowances
- Selection of suitable anode metal (zinc, magnesium, aluminum, iron, mild steel or other metals anodic to the protected structures or equipment) and its alloying composition
- Requirements for introduction of current control to limit output within the optimum parameters
- Selection of the size of anodes to provide optimum life
- Selection of the suitable shape of anodes to secure optimum spread
- Determination of the total number of anodes required
- Anode spacing to give uniform current distribution

- Selection of test-point localities
- Attachment of anodes. Note: Sacrificial anodes should be conductively attached to the protected metal, but their sacrificial mass should preferably be separated from the protected surfaces.

A typical basic appreciation of cathodic protection by impressed current/cathodic control is as follows:

- Estimate of total current requirements
- Resistivity of water, soil, or electrolyte solutions
- Requirements for insulating flanges and bonding to foreign structures and equipment, and assessment of extra current allowances.
- Selection of suitable groundbed locations (in low-resistivity soils or media, reasonably near power supply, at points where there are no interference problems, where beds and cables are reasonably secure from interference or disturbance)
- Decision on the type of anodes and the design of their attachment
- Decision on whether the anodes (if elongated ones selected) should be installed vertically or horizontally
- Decision on the voltage to be used
- Determination of the optimum anode material
- Optimum number and size of the anodes
- Decision on anode spacing
- Type and location of reference electrodes
- Requirements and design of grounding of propeller shaft, rubber, and other attached substructures and equipment within the protected complex – materials and systems
- Location of controllers, power supply, and transmission (cabling and installation)
- Potential hazards of marine and surface traffic
- Wave action and soil instability
- Bottom involvement
- Weed fouling and microbiological effects
- Malicious damage.

Where cathodic protection is to be used the alkali resistance of the protective paint coatings should be evaluated. Where possible, cathodically protected surfaces should be preserved by suitable surface coatings or linings. All precautions should be taken to prevent hydrogen embrittlement of high-strength metals arising from their cathodic protection.

Detailed design of cathodic protection systems is a highly specialized field of expertise and should be left primarily to a corrosion specialist. However, it will be the designer's task to accommodate, eventually, the diagrammatic detailed design rendered by the corrosion specialist in the functional design of the utility to their mutual satisfaction.

Use of zinc-rich primers on cathodically protected structures or equipment in a conductive environment is not generally recommended.

A typical basic appreciation of anodic polarization by impressed currents/anodic control is as follows:

- Estimate of total current requirements
- Is the used chemical/metal system suitable for anodic polarization (e.g. oleum and carbon steel, cold concentrated sulfuric acid and carbon steel, hot concentrated sulfuric acid and stainless steel, dilute sulfuric acid and stainless steel, etc.)?
- Conductivity of liquid, its temperature, pH, pressure, and velocity
- Minimum, normal, and maximum concentrations of the liquid

- Is any substance present which might coat, abrade, or coagulate?
- Decision on the type of the cathodes and design of their attachment
- Decision on the voltage to be used
- Selection of the optimum cathode material
- Optimum number, size, and spacing of cathodes
- Type and location of reference electrodes
- Location of controllers, power supply, and transmission
- Potential fouling of cathodes and reference electrodes.

10.2.4 Protection by Adjustment of Environment

Reduction of corrosion by a change of environment should be considered, provided the design is suitable, and this can be achieved without excessive cost by any one, or several, of the following methods:

- Lowering the corrosiveness of the atmosphere or other corrosive media by ventilation, dehumidification, air conditioning, reduction of acid strength, sacrificing chemical efficiency for the sake of lower corrosion costs, continuous venting of steam from the unit, reduction of concentration of CO_2 and oxygen in condensate, etc.
- Adjusting the thermal efficiency of the components by raising or lowering the temperature by reduction of thermal efficiency of preheaters and boilers, by making heat exchangers co-current instead of counter-current, by reduction of peak metal temperature, etc.
- Using the inhibitors in critical media, e.g. fuels, process liquids, cooling waters, paints, elastomers, etc.

A typical basic appreciation of ventilation, dehumidification, and air conditioning for change of environment is as follows:

- Requirements for habitability
- Adjustments of environment to improve protection through control of corrosiveness
- Corrosion rating of particular design complex.

Desiccating agents used in corrosion prevention must be cheap, easy to handle, and non-corrosive. Easy access for inspection and replacement must be provided and eventually provision for regeneration *in situ* should be made.

A typical basic appreciation of inhibitors for the purpose of change of environment is as follows:

- What is the effect of inhibitor concentration on corrosion rate?
- Minimum concentration needed
- Tendency to favor pitting – effects at water line
- Relation to surface area of metal – initial consumption (in coating surface, in reacting with existing corrosion scale)
- Effectiveness as a function of time
- Tendency to be consumed by reaction with ingredients of the corrosive medium
- Effectiveness under varied conditions that may be found in plant (different temperatures, concentrations of corrosive, velocities, aeration, etc.)
- Effectiveness on metal already corroded
- Can the cost of maintaining a sufficient quantity of inhibitor in the system, and the cost of testing that this quantity is being maintained at an appropriate level, be kept within reasonable economic boundaries?

- Can the inhibitor contaminate the product/contents?
- Can the inhibited fluid present an effluent problem?
- Can the inhibitor loosen corrosion deposits and thus cause blockages?
- Can the inhibitor precipitate on stream and is the sludge or scale thus formed acceptable?
- Can the organic inhibitor coat the surfaces too heavily, to the considerable detriment of efficiency of heat transfer and filtration, or can it give undesirable emulsification, iron exchange, etc.?
- What effect will it have on other metals or bimetallic couples that may be present?
- Can the inhibitor cause foaming and thus impair the operation?
- What are the hazards in handling toxicity?
- What would be the cost and effect of a fall in the inhibitor concentration?

The combined effect of inhibitors and cathodic protection is far greater than the individual effect of each method separately. Avoid packaging materials containing soluble salts or acids in significant quantities or emitting corrosive vapors. Prevent entrapment of gaseous contaminants carried by air between the metallic components and the packaging materials.

10.2.5 Protection of Structures

- Anodic metallic coatings have proved their economic value for the protection of capital structures (galvanized, metallized, zinc-rich paints).
- However, where the use of metallic coatings is contemplated for protection of strength structures, attention should be given to the problems of ageing, cracking, diffusion, corrosion, and hydrogen embrittlement (this is due to both the method of surface preparation and the development of gaseous hydrogen by the cathodic protection process).
- Metallic coatings used under insulation should always be well sealed and protected.
- Zinc coatings have a good corrosion resistance in most neutral environments, especially if passivated. Zinc coatings without sealer should not be used in corrosive conditions (marine and industrial environments), in totally unventilated spaces and in proximity to electronic equipment subject to phenolic vapors emanating from insulating materials, varnishes, or encapsulates.
- The average thickness of zinc sprayed on structural steel is normally 76 µm (3 mils); in corrosive conditions up to 153 µm (6 mils) thickness is used. The average weight of zinc applied by galvanizing on structural steel is 61 mg/cm^2 (2 oz/ft^2).
- Aluminum coatings (910.5% commercial purity aluminum) have a good corrosion resistance to marine conditions, industrial atmospheres, weak acids, etc.; layer corrosion of heat-treated aluminum can be completely stopped by a hot sprayed aluminum coating (the main impurity must not be copper) of its surfaces. Coupling of thus-protected structures to copper, lead, or other noble metals is not normally recommended.
- The average thickness of hot sprayed aluminum on structural metals (steel, aluminum) is normally 102 µm (4 mils); for immersed conditions up to 203 µm (8 mils) of aluminum spray can be specified.
- All provisions must be made in the design for application of a uniform thickness of protective metallic coatings.
- Cadmium metallic coating is superior to zinc coating for stain and tarnish resistance in rural environments. In marine conditions its resistance is uncertain. Chromate posttreatment should be used. Cadmium coating should not be used in totally unventilated spaces and in proximity of electronic equipment subject to phenolic vapors emanating from insulating materials, varnishes, or encapsulates.
- Lead coatings have good corrosion resistance to sulfuric acid and to industrial atmospheres without chlorides or nitrates.

- Cathodic metallic coatings should not be used on submerged and underground structures subject to physical damage and abrasion.
- Areas of structural metals affected by cavitation can be surfaced with welding wire or strip, overlay welding, or coating with dense high-tensile materials that resist cavitation damage (e.g. chromium stainless steel 18-8).
- Thermal-sprayed coatings are not homogeneous isotropic entities, and they do not have the same properties as identical bulk materials:
  - Passage through flame or arc causes preferential oxidation.
  - Contaminants are picked up.
  - Strength is lost and coating may become embrittled.
  - Reaction to heat treatment changes.
  - Thermal conductivity changes.
  - Porosity of coating influences fracture behavior.
  - Bond adherence varies.
- Perform detailed analysis of local environmental conditions prior to undertaking activities appertaining to selection of protective systems.
- Weathering, etching, hot phosphating, or priming with calcium plumbate should be specified prior to application of sealer or paint on top of galvanizing.
- Appropriate cleaning, etching, or priming with zinc chromate primer or barrier coat should be specified prior to application of sealer or paint on top of hot sprayed metal or zinc-rich primer.
- Due consideration should be given to any adverse effect of the coating on the metal substrate or metallic coating (e.g. lead- or copper-containing compounds should not be applied on top of solid or coated zinc or aluminum). This applies also to application over zinc-rich primers.
- Prefabrication treatment of structural metals, critical strength permitting, is recommended. Fabrication procedures must be fitting to the use of prefabrication-treated metals.
- To facilitate application and inspection, select individual and different colors or tinting of successive coats within a paint system.
- High duty paints and compositions should be specified for protection from corrosive fluids, in less accessible spaces, and for protection of the cathodic metal in a galvanic couple.
- Postassembly and postpainting flame cutting and welding should be reduced to a minimum. Specify restoration of damaged coatings to their original integrity.
- Provide against any unnecessary damage to coatings applied at the preassembly stage.
- Aluminum or aluminum coatings should not be anodized if electrical conductivity is required.
- Fully heat-treated aluminum alloys, prior to painting, should be primed with chromate primer containing not less than 20% zinc chromate pigment.
- Cathodic protection dielectric shields should have good insulating qualities, low permeability, good adhesion, and good alkaline resistance. The shields should be of sufficient size to prevent damage to the adjacent coating system and ensure good current distribution. It is recommended that the coating thickness of the adjacent paint coating be increased in the immediate periphery of the shield.
- The limit on polarization level to below –1 V (Ag/AgCl) is valid for marine coatings, including zinc primers used together with cathodic protection systems.
- Environmental anti-pollution regulations and health precautions should be incorporated into specifications and design:
  - Cleaning of materials – in-shop cleaning, vacublast, wet blasting
  - Supply of raw materials (paints, solvents) – non-toxic or reduced toxic contents.

- Design parameters for selection of coatings of hydrodynamic structures are as follows:
  - Frictional resistance (relative speed, wetted surface area, surface roughness).
  - Wave and eddy resistance (from total resistance obtained by tests in hydrodynamic tanks subtract frictional resistance).
- Concrete structures lying in waterlogged ground should be protected with sealing membranes (e.g. a high build bituminous composition on top of primer).
- Piles and structures to be enveloped or jacketed should first be cleaned and freed of all contamination and fouling. Surfaces to be jacketed should also be, by preference and if possible, primed with anti-corrosion composition prior to jacketing.
- Prior to application of corrosion inhibiting or insulating wrapping tapes to structural steel, the steel should be thoroughly cleaned and primed, tubular structures wrapped, and structural shapes taped longitudinally. The tape should be well pressed down and smooth, and the tension should not be excessive. Folds and air pockets should be avoided; the tape over protruding nuts, bolts, etc., should be cut in the form of cross, with the tape pressed firmly to the metal and the exposed surface patched up with a piece of tape (see Figure 10.20).
- Surfaces exposed to serious damage by abrasion or repeated impact in corrosive conditions may be protected by loosely hung or bonded rubber liners in the required thickness, 6 mm thick and up. Edges and metal surfaces covered by loose lining should be protected against corrosion (see Figure 10.21). Loosely hung or bonded rubber liners may protect surfaces exposed to serious damage by abrasion or repeated impact in corrosive conditions.
- Use of precoated, in-factory or in situ plastic clads and simple or complex plastic laminates (e.g. fibrereinforced plastic laminate, polypropylene sheet with glass fibre cloth, etc.), for the fabrication of suitably designed corrosion-resistant structures should be evaluated.
- Design changes from standard on pristressed concrete water reservoirs:
  - Cable-stressed reservoirs – use airtight flexible metallic conduit for horizontal encased cables.
  - Bar-stressed reservoirs – fill the vertical coupling beams with cement grout on construction; apply minimum 5 cm (2 inches) cover of cement mortar over bars and beams.

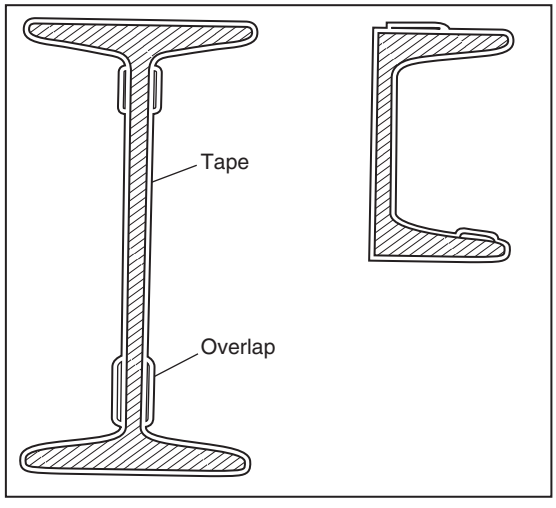


Figure 10.20 *Insulating wrapping tapes. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

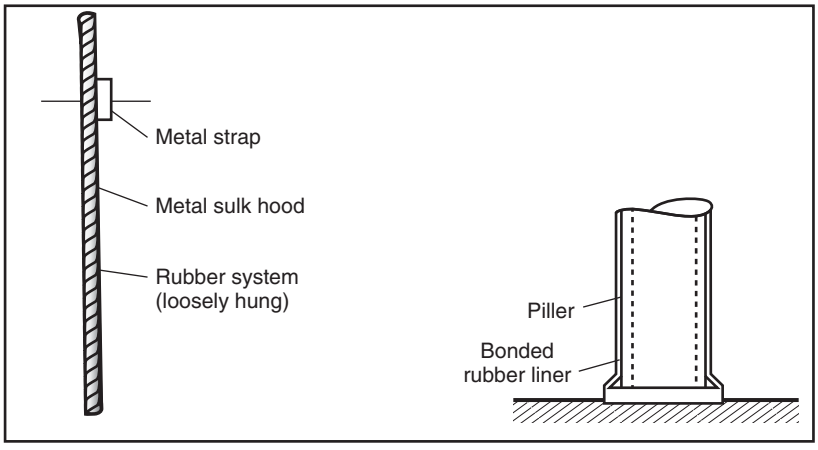


Figure 10.21 *Edges and metal surfaces covered by loose lining should be protected against corrosion. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

- Wire-stressed reservoirs – no cavities round wires caused by their bunching; apply cement slurry coating just before and after wrapping operation; mortar uniform in density, minimum 5 cm (2 inches) for unpainted surfaces and 2 cm (¾ inch) for painted surfaces; mortar thoroughly moist during curing period; sealing coat applied as soon as possible after curing; if back-filled, exterior wall to be sealed.

- Basic requirements for obtaining optimum result from protective coatings:
  - Optimum geometry for cleaning, application, inspection and maintenance of the coatings; also geometry for upkeep of coatings in good protecting condition.
  - Optimum knowledge of materials and methods of protection, close collaboration with reputable suppliers or consultants.
  - Optimum and accurate specification of coating systems; comprehensive detail of specified matter, coating engineering.
  - Use of reputable or approved contractors or applicators; trained and competent personnel; preferably under cover.
- Use of optimum inspection methods; complete inspection throughout.
- Attachment of sacrificial anodes to galvanic couples:
  - Brings potential of cathode to the level of anode and then reduces the whole to potential of the couple (danger; excessive formation of zinc oxide)
  - To be used when excessive formation of zinc oxide is to be avoided (problem of space and operation) or in closed pipe systems.
- Alternative protection of fasteners in design by sacrificial action of dissimilar metal:
  - Structural carbon steel is sacrificial and protects the fasteners – this design can be used where the excess weight can be added to the established design requirements, corrosion and pitting of the steel will not be detrimental to the function and the structure is not highly stress loaded.
  - The sacrificial anode is the sacrificial metal that protects both the fastener and the structural steel – this design should be used on structures in conductive environments that are subject to

weight limits, where corrosion and pitting would interfere with movement of operations and where the corrosion or pits could form stress-raisers on structures under critical stress loading.

- In design of pristressed concrete water reservoirs or underwater reinforced concrete tunnels for future installation of cathodic protection, all metallic members of the structure, including wires, reinforcing bars in the walls and the floor, interior ladder, piping, and vertical stressing rods should be bonded together.
- General performance of applied cathodic protection by sacrificial anodes can be evaluated as follows:
  - Anode variables – material composition, manufacturing method, physical shape, electrical contact via the anode output, anode capacity, anode efficiency, anode potential.
  - External variables – area of bare metal to be protected, system life or length of protection, chemical composition of electrolyte, temperature of electrolyte, flow rate of electrolyte, aeration of electrolyte, position of anode in space relative to metal work.
  - Design variables – area of metal work to be protected, type of coating, length and frequency of time the metal work is in contact with electrolyte, required life of system, selected current density.
- A centrally located anode is twice as efficient as one mounted at one end of the structure. Two symmetrically located anodes are about 1.6 times as effective as a single anode. Where more anodes are used, the efficiency increases and the total current requirement is reduced.
- Avoid using too few high output anodes; relatively poor distribution efficiency increases the requirement of current (applies to sacrificial anode and impressed current systems).
- Avoid locating anodes in groups close together.
- Provide for electrical continuity of all metallic components, in immersed structures, that are cathodically protected.
- Avoid over-protection of cathodically protected structures; this could cause peeling of protective paint systems and also hydrogen embrittlement, especially of high-strength steels.
- A combination of coating and cathodic protection is required for effective protection of submerged structures.
- Bare inorganic zinc coatings should not be used together with the cathodic protection systems in submerged conditions (sea or brackish water). This applies also to painting of bilges protected with sacrificial anodes.
- Sacrificial pieces should be used on critical structures subject to heavy corrosion loading, even when the whole structure is protected by cathodic protection overall.
- Trailing anodes provide the advantage of a uniform potential field distribution.
- To prevent galvanic corrosion of bimetallic structures, the concentration of inhibitor should be increased as compared with protection of a single metal structure.

10.2.6 Protection of Equipment

- Where good corrosion resistance is required nickel coatings can be used for protection, particularly in chloride-free atmospheres and in highly alkaline conditions. Use of chromium over nickel improves appearance and corrosion resistance.
- Chemical-resistant compositions of glass can be used as a coating for air-heater element plates, tank heating coils, air-heater tubing, economizer tubing, economizers, etc.
- Avoid specifying and designing dry working surfaces for exposed fittings (e.g. door clips) – specify suitable lubrication.

- Parts that are totally and continuously immersed in oil or grease (preferably inhibited), and those embedded in encapsulate or moisture-proof compound, need not necessarily be given any further protection. Local application of oil or grease, however, does not automatically provide good corrosion protection.
- Dip-coating in suitable plastics may be used for submerged mild-steel equipment exposed to high pressures and relatively low temperatures.
- Use of precoated and plastic-clad metals may be considered for production of equipment cabinets.
- When impingement of surfaces by vapor bubbles or erosion by abrasion action is possible, lining surfaces with loose or bonded elastomers may be considered. The surfaces of equipment to be so treated must be clean, smooth, and preferably inhibited or coated with anti-corrosion coatings. The thickness of the lining depends upon flow and impact energy. Screwed joints should be avoided.
- Tanks to contain corrosive liquids may be completely or partially lined with bonded or independent flexible laminated plastic liners. Ingress of corrosive liquids to the interface between the elastomer liner and the metal must be prevented.
- Under optimal conditions some surface coatings can serve several purposes, i.e. corrosion prevention, electrical neutrality, and chemical inertness, self-cleaning and lubricity. Balanced evaluation of the particular design is necessary.
- The use of coatings and linings for absorption or attenuation of noise should be considered.
- Cathodically protected equipment should not be over-protected as this may cause peeling of paint and hydrogen embrittlement of high-strength steels.
- Both painting and cathodic protection are mostly required for protection of submerged equipment.
- Critical equipment should be protected locally by sacrificial pieces, where exposed to heavy corrosion loading.
- Cathodic protection of condenser boxes and other heat exchangers using natural waters is a necessity.
- Cathodic protection of inhibited recirculating cooling water systems (copper tubes, steel tubesheet) can be effective if:
  - Sodium-zinc molecularly dehydrated glassy phosphate inhibitor is used
  - Overhang of the copper tubes in the sheet is below 6 mm (1/4 inch) for 19 mm (3/4 inch) diameter tubes on 25 mm (1 inch) centers
  - Magnesium anodes located 30 cm (12 inches) from tubesheets are used and their shape is optimal.
- Provide for admittance of sufficient air to the flowing fluid to relieve local or general low-pressure areas and so eliminate causes of cavitation.
- Provide feed water treatment on cooling towers or evaporative condensers by disposable chemical cartridges, where suitable, or by other means.
- Provide for intake of unpolluted air into internal combustion engines, gas turbines, and boilers. Demisters, filters, chemical filters, preheaters or air dryers may be required to remove adverse solid, liquid, or gaseous pollutants.
- Provide for supply of clean and unpolluted lubricants and propulsion fuels to propulsion machinery and other plant. Filters, coalescer-filters, etc., may be necessary to remove solid, liquid, or gaseous pollutants.

10.2.7 Protection of Pipe Systems

- Metallic coatings can be used not only for protection but also for simplification of surfaces, electrical or thermal conductivity, avoidance of crevices etc. (

- Selection of buried pipelines coatings is based on the following requirements:
  - Highest insulating resistance over the entire operating service life
  - Resistance to deformation stresses along the weight-bearing surfaces
  - Resistance to temperature (high and low) deformation forces
  - Chemical inertness to water-soluble electrolytes
  - Insolubility in petroleum crudes, derivatives, and solvents
  - Resistance to microbiological attack
  - Optimum economy
  - Easy maintenance.
- Residual stresses introduced into pipe weldments by fabrication processes are aggravated by hot dip galvanizing.
- Pipes up to a 5 cm (2 inch) bore can be lined, normally in lengths up to 3 m (10 ft), with rubber where required; larger bores can be lined in lengths up to 6 m (20 ft). Standard flanged-bolted-type pipework can be used for rubber lining; screwed joints are generally not satisfactory. Elbows, bends, and tees can also be lined. Normally the substrate surfaces should be clean, metallized or primed prior to application of a rubber lining.
- Pipelines encased in or coated with concrete should be separated from pipelines buried in soil, whether these are bare, coated with insulating-type materials, or insulated (see Figure 10.21). Appropriate insulating devices should be used for separation. If such precautions are not possible, compensating cathodic protection should be used.
- For design of mortar-lined-and-coated steel pipes.
- Where no coatings are used on the cathode surface of a closed system, the area of optimum protection should cover a 2.5:1 spacing. If the closest anode to cathode spacing is 0.3 m (1 ft) and a potential of 1000 mV is obtained, a potential of at least 850 mV will be achieved at 0.75 m (2.5 ft) distance from this anode.
- At a surface velocity of 0.3 m/s (1 ft/s) over a smooth metal surface, a current density of 2.2 A/m^2 (200 mA/ft^2) will protect steel, stainless steel, and copper-based alloys.
- A single sacrificial anode attached to one end of a pipe can normally, and in freshly piped seawater, protect the internal surfaces of a pipe only up to 2–3 diameters in depth and installation of a continuous strip anode may be required. In stagnant seawater, however, even 12–50 mm (0.5–2 inches) nominal diameter stainless steel (e.g. Type 304) and copper pipes can obtain effective cathodic protection after an initial polarization period, which can vary between four days, for 5 cm (2 in) diameter stainless steel pipe, and 186 days for 12 mm (0.5 inch) diameter copper pipe, by a single sacrificial anode fitted to one end to a depth of approximately 6 m (20 ft).
- A sacrificial anode is not normally effective in the crevice between two pipe flanges. Either one of the flanges should be made sacrificial and the dissimilar metals left in contact, or if only the apparent surface of the crevice is be effectively protected, the supply of protective current into the crevice may not be necessary.
- Plastic- or rubber-lined pipe systems should be designed for the least exposure of unprotected edges to corrosive environments (submerged or spillage).
- Typical arrangement of cathodic protection in ground bed installation: $d = 6 - 9$ m (20–30 ft), depending on soil resistivity and availability of space; 3–21 anodes in ground bed.
- Condensation on external surfaces of piping systems should be prevented by the appropriate application of insulation and ventilation.
- Provide for removal of oxygen from feed water and keep the oxygen level within the required limits; this is to eliminate corrosion and pitting in boiler tubes.

- Where a differential of temperature could affect the corrosivity of the environment or cause adverse stresses in materials, provision for adjustment of the temperature of the transported liquid should be made.
- Where liquid is being transported through pipes made of active/passive metals, natural or forced oxygenation of the liquid may be necessary for renewal of the protective films and also for release of H_2S.
- For removing corrosive particulates and soluble gases from ducted exhaust air streams, wet cyclone scrubbers, or spray towers or chambers should be introduced into the system.
- Where metals or other minerals dissolved in water could adversely affect the piping systems and equipment, distillation of the water, chemical treatment, or electronic treatment may be necessary.
- The concentration of inhibitor used for prevention of galvanic corrosion in pipe systems should be increased, as compared with protection of single metal.
- For optimum protection of pipe systems, a combination of resistant materials, low contents of corrosive gases in liquids, chemical treatment for passivation of metal surfaces, low erosion and impingement geometries, suitable velocities, and cathodic protection may be required.
- Corrosion prevention by means of controlled scale deposition (uniformly thin), regardless of different temperatures occurring in the system on both cool and hot surfaces, is attractive, and can be achieved by eliminating inhibitors, using the appropriate chemicals, and by selecting suitable ranges for scale-forming constituents.
- Design for avoidance of biological fouling in seawater systems as follows:
  - In intermittent service provide against dead organisms clogging restricted passages.
  - In critical systems design for water velocity of more than 1.8 m/s (6 ft/s), but less than one that may cause damage to the system.
  - In critical systems provide smooth internal surfaces without porosity and physical damage – line with soft rubber, if possible.
  - In critical systems the design of critical surfaces should allow either for access of light or be light-colored, if possible.
  - In pipe systems made of high-content copper metals, no residual deposits of resin, pitch, or pollutant should remain; stainless steel should be flushed after each operating period; plastic should be restricted to intermittent service.
  - Where the above measures do not help, arrange for a periodic raising of the temperature to over 38 °C (100 °F), or introduce a massive dose of chlorine.
- Fouling of internal surfaces of pipe systems by contained solids can cause heavy corrosion and erosion. De-sludging, sedimentation, clarification, and filtration arrangements should be made.
- The employment of fouling monitors to check the effectiveness of physical and chemical filtration, and antifouling precautions is recommended.
- To prevent re-ingestion of solids and micro-organisms from discharge units into the intakes of pipe systems, only clean and safe effluent should be discharged.
- Desludging, cleaning, and de-watering of lubrication and fuel oils (including diesel oil) should be undertaken for reduction of corrosion.

10.2.8 Protection of Electrical and Electronic Equipment

- The following techniques are mostly employed to prevent deterioration of electrical and electronic equipment:
  - Protective coatings

  - Encapsulation
  - Evacuation of air, followed by hermetical sealing (units)
  - Filtering of air-removal of gaseous pollutants and solid particles
  - Exclusion or effective removal of moisture
  - Air conditioning – continuous maintenance of optimum environmental conditions.

- Iron and mild steel used in electrical and electronic equipment is normally coated with cadmium, nickel, or tin, except in the following circumstances:

  - Precision parts that are totally and continuously immersed in oil, grease, encapsulant, or moisture-proof coatings, or those contained in hermetically sealed units (i.e. sealed hermetically by fusion of metals, glass, or ceramics), need not be given other protection; local application of oil or grease should not be taken as adequate corrosion protection.
  - Laminations used in magnetic circuits need not be plated if otherwise protected from corrosion.
  - Springs should, by preference, be protected by organic coatings or by metallic coatings applied by vacuum deposition or other non-hydrogen-producing processes, rather than by electroplating.
  - Structural parts of electrical and electronic equipment should be cleaned, metallized or primed, and painted.
  - Close tolerance parts not exposed to outdoor atmospheres should be protected by corrosion-preventive compounds.

- Aluminum and its alloys should be anodized and painted, except in areas of electrical bonding. In such areas and where anodizing is not possible, a chemical film treatment may be used, although it does not afford corrosion protection equivalent to anodizing. When possible, chemical films should be given the additional protection of organic coatings.
- For those applications where aluminum or its alloys are involved in continuous exposure to elevated temperatures, where the resulting oxide build-up would be objectionable (e.g. heat sinks), metallic coatings with suitable thermal characteristics should be considered in place of anodizing.
- Copper and copper alloys may be given a black oxide treatment, plated, or painted.
- Magnesium, when its use is essential, should be protected as follows:

  - Rigid magnesium parts should be anodized – those subject to flexing should be chemically treated.
  - All magnesium parts should then be given two coats of alkali-resistant primer, followed by one or more coats of a compatible top coat; magnesium parts for electronic applications may be given other moisture-proofing coatings (epoxy, polyurethanes) in place of the primer and top coating.

- The noble metals, i.e. gold, platinum, palladium, and rhodium, and the corrosion-resistant metals, i.e. chromium, nickel, tin, tin-lead solder, and titanium, require no finish other than cleaning.
- Soldered joints should be protected with a moisture-proofing compound or coating.
- Corrosion-resistant (or treated to resist corrosion) minor devices (fasteners, etc.) should be used. Fasteners should be treated with zinc chromate, zinc chromate paste, or graphite-free dry-film anti-seize compound.
- The joint area of the electrical bond should be provided with a protective finish after bonding (organic coating, sealant, paint system).
- Metallic coatings should be selected for their suitability for the application involved, attention being given to the problems of ageing, diffusion, and corrosion and selected as follows:

  - Cadmium or tin are used on metals that will be in contact with aluminum or magnesium.
  - Cadmium or tin are used as a pre-paint coating.

  - Rhodium over silver; gold over silver, copper or nickel; and nickel between copper and silver are applicable where tarnish prevention is required.
  - Heavy gold 0.762 μm (0.03 mil) thick is used where subject to marine exposure.
  - Tin, gold, or tin-lead are used for soldering.
  - Gold, rhodium, or reflowed heavy tin are used for storage.
  - Chromium, nickel, rhodium, or hard gold are used for wear.
  - Cadmium, nickel (in ferric chloride only), indium, or tin are used for easy etching.
  - When base metals intended for intermetallic contact form non-compatible couples, these should be plated with those metals that will reduce the potential difference.
  - Heavy metal coatings should be used in preference to thin coatings.
  - Where practicable, gold, platinum, or tin-lead coatings should be used in preference to silver.

- Metallic coatings that may be applied by vacuum deposition to metallic or non-metallic surfaces for electrical conductivity should not be used for any mechanical application, due to their extreme thinness, fragility, and susceptibility to damage.
- Use of cadmium plating for enclosed assemblies containing acids, ammonia, organic coatings, adhesives, plastics, varnishes, or other organic materials subject to heat, or their vapors, should be avoided.
- Avoid use of palladium plating in enclosed assemblies containing organic materials to prevent polymerization.
- Hot dip tinning should be used instead of electrodeposited tin; tin-plating should be reheated to relieve stresses.
- The formation of copper oxide corrosion in pin-holes in metallic plating over copper should be prevented by interposing a layer of nickel between the copper and the top plating film.
- Silver plating should be protected from sulfurous fumes on storage and it should be cleaned immediately prior to soldering.
- Zinc plating should not be used.
- The thickness of gold plating should be sufficient to minimize porosity and provide complete corrosion protection. Recommended thicknesses are as follows:

  - For tarnish prevention of silver, 1.27 μm (0.05 mil).
  - For waveguides or contacts where a non-migrating material is required 2.54 μm (0.10 mil).
  - For general engineering use, 5.1 μm (0.20 mil).
  - For resistance to extreme corrosion and wear, 7.62 μm (0.30 mil).

- Special care should be taken to prevent or retard the diffusion of substrate metals (silver, copper, chromium) into electrodeposited gold under high-temperature conditions. A suitable barrier to prevent diffusion is a thin nickel or palladium coating between the gold plating and the substrate.
- Soldering over gold should be avoided whenever possible. Where necessary, care should be taken to minimize the formation of brittle gold solder compound by one or more of the following methods:

  - Using extremely pure (910.99 + %) gold
  - Using thin plate
  - Using minimum soldering time at minimum temperature.

- Metallic coating may be applied to non-metals to provide a conductive surface. Although some problems (e.g. dissimilar metals corrosion) are thereby minimized or obviated, other corrosion reactions of the metal coating should be considered in the same manner as for plated or solid metals.

- Attachment of conductive plastics (filler types: silver flake, gold dust, pure carbon- or metal-plated types) for the purpose of establishing necessary electrical contact should be engineered to suit the form of the product.
- The ideal coating for an electrical circuit (jelly-type, foam-type, rigid, elastomeric, aerosol-type varnishes) shields it from environmental conditions mechanically, electrically, and chemically without affecting the circuit's original characteristics. The coating should serve the following basic purposes:
  - Environmental protection to seal out moisture and other airborne contaminants, especially salts and sulfur compounds
  - Handling protection to prevent damage from hand-borne contaminants (salts, oils, sulfur compounds) that are deposited on the component during the final assembly or field testing
  - "Ruggedization" against shock or vibration for protection during in-plant handling, testing, and final use
  - Insulation protection to maintain the electronic circuitry in a condition very close to its sterile design environment.
- Organic or inorganic coatings, when used, should be compatible with the substrate.
- Protective coatings should be applied after all punching, drilling, machining, forming, and fabrication have been completed. Paint finishing systems, if required, may also be applied after metal deposition or over chemical film treatment.
- Corrosion-resistant steels should be passivated. No further finish is required to provide corrosion resistance to 300 series steel; where tarnish, rust, or surface stain would be objectionable, the 400 series and precipitation hardening steels should be given additional protection by a suitable plating or, after passivation, receive one coat of zinc chromate primer followed by a suitable top coat.
- Soldered joints should be moisture proofed and the joint area of an electrical bond should, after bonding, be provided with a protective finish (organic coating, sealant, paint system). All contaminants should be removed from conductor surfaces.
- Direct corrosive environment away from critical equipment by judicious use of drainage and ventilation.
- Condensation should be precluded, by keeping components at temperatures above the dew-point.
- Unless specified otherwise, the moisture level inside electronic equipment should be maintained below 30% RH at 20 °C (68 °F).
- Moisture should be further excluded from electronic devices by adequate housing, seals, gaskets, and closures.
- Hygroscopic materials should be avoided. Desiccants should be used as little as possible, and then should not be in contact with unprotected metallic components.
- Contaminants should be removed from cooling air before it enters electronic equipment.
- Conductors should be provided with organic moisture barrier coatings where necessary.

10.3 Maintenance

It would be a truly ideal achievement to provide, in design, for absolute functional reliability of a utility during its full operational life – from its conception to the termination of its usefulness. This, however, will be only very seldom possible in practice, and the designed structure or equipment may fail as a result of random catastrophic failures of individual parts or by progressive degradation and

deterioration of performance. Corrosion-control assessment should take account of both catastrophic and degradation failures with the understanding that each can be caused by a conglomerate of both mechanical and corrosion factors.

The designer can expect that during the utility's operational life its failures, including the failures of intrinsic corrosion control, will proceed in three stages. In the first phase, representing the debugging period, the failure rate will rapidly decrease from an initial peak, due to replacement of parts, correction of design, and practical manufacturing and preservation errors.

In the second phase, a constant failure rate of lower power can be expected and this can be further reduced to the lowest possible frequency and potential by the diligent effort of designer and corrosion specialist. In this way the period of the utility's usefulness can be extended to the most economic length of time, with the help of operational maintenance, when necessary.

In the third, or wear-out phase, the incidence of failures will again rise through a combination of catastrophic and deterioration failures. It is again in the hands of the above-mentioned group of specialists to postpone this period to the ultimate end of the utility's useful life.

Every designer should acquire an eye for a design form that is economically maintainable, and also maintain a sympathetic understanding of the problems met by maintenance crews and endeavor to make their task as simple and cheap as possible.

10.3.1 Requirements

When failures occur, the cost of major repairs, the danger of pollution of contents by corrosion products, the loss of productivity, the danger of destruction of a utility, and of human life should in most cases, enforce some sort of operational or preventive maintenance. As long as the equipment has to be maintained, its maintainability must be ensured. Followings are the major tasks to be considered with respect to maintainability.

All corrosion-control precautions included in design should be "inspectable." Their temporal state and efficiency should be open to observation under the conditions given by the selected geometry of the utility, its location, and its arrangement, and this should be possible in the ambient environment of production, operation, or maintenance, and with reasonable ease.

All specified corrosion-control precautions should be "repeatable and repairable" with reasonable ease in the given position and environment, as far as possible.

The preference of replacing the whole utility (or its individual parts) instead of repetitive maintenance should be assessed on the economic and operational conditions of the utility.

Fundamental changes in the design concept may be necessary to avoid major impediments in maintenance, especially on complex structures and equipment in a corrosion-prone environment.

Anti-corrosion maintenance should either require the shortest possible length of time to be executed, or it should be as widely spaced as possible (e.g. in the case of structures and equipment or parts located of necessity in inaccessible positions). The design should be based on the optimal length of corrosion prevention.

The anti-corrosion maintenance should lend itself to a planned maintenance program, which should be implemented with the least interference to the operation or use of the utility, and at the same time be compatible with corrosion incidence. Periodicity of maintenance should suit the operational cycles to cause the least possible inconvenience all round.

All precautions should be taken in design to reduce the cost and degree of difficulty of subsequent maintenance, including dismantling and reassembling of structures and equipment, cleaning and preparation of surfaces *in situ*, preservation, etc. to a minimum. All such operations should be made easy and foolproof.

The safety of the maintenance personnel should be given due consideration (e.g. easy and adequate access with tools, provision of maintenance platforms, temporary ventilation, lighting, etc.).

Fast-corroding and critical parts should not be located in inaccessible positions within a utility, which would involve maintenance personnel in major dismantling operations. Such parts or units should be easily removable. Parts requiring difficult anti-corrosion maintenance should not be positioned in dark places.

Materials and protective systems should be selected with an inherent economic length of resistance to corrosion. Anti-corrosion maintenance should be adjusted to suit problems arising from engineering maintenance procedures (e.g. physical damage, spillage of chemicals, etc.).

Accessibility for inspection should be reconciled with the selected inspection and destructive or non-destructive testing procedures (e.g. X-rays, ultrasonic, visual, probes, instruments, etc.). Probable expertise and availability of future maintenance personnel may govern selected maintenance requirements. The use of modular assemblies tailored to the requirements of corrosion control is recommended.

10.3.2 Structures and Equipment

Obstructions to maintenance of the structure or equipment should be sub-divided, where necessary, and their width should be kept to a minimum. The optimum distance of an obstacle from the background structure or equipment depends on the available and required maintenance equipment and technique.

Excessively low inaccessible seatings for machinery and equipment should be avoided, especially if entry or accumulation of an unwelcome electrolyte within their frame is possible. Coverplates and other items that have to be removed for maintenance purposes should be readily detachable .

Critical equipment subject to a corrosive environment may need to be arranged to accommodate corrosion coupons, probes, and corrosometers (see Figure 10.22).

Piping systems should be designed to be cleaned on-stream, if possible and necessary. Critical parts or parts of systems subject to heavy corrosion should be separately dismantleable. Blind or non-inspectable areas should be kept to a minimum in a fail-safe design and, where unavoidable, additional strength must be provided to prevent the critical effects of corrosion fatigue.

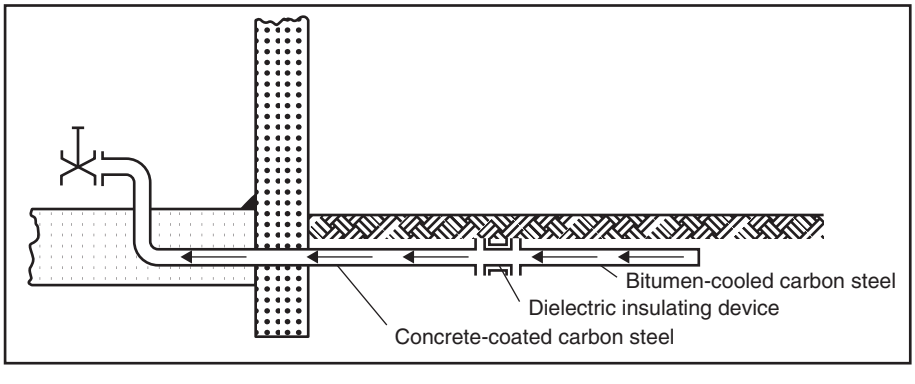


Figure 10.22 *Pipelines encased in or coated with concrete should be separated from pipelines buried in soil. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

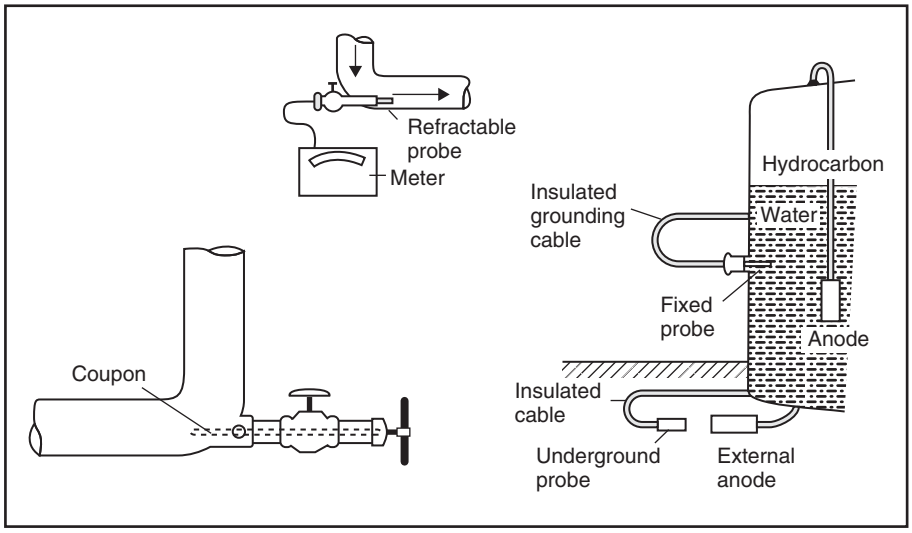


Figure 10.23 *Arrangement to accommode corrosion coupons, probes, and corrosometers. (Reproduced with permission from Wesfarmers Chemicals, Energy & Fertilisers.)*

10.4 Economics

Corrosion, as such, is basically an economic problem associated closely with the loss of capital assets and business profits; corrosion control should provide the most advantageous course of obviating such losses in the first case, whilst not neglecting the most important implications of safety, health, pollution of environment and products, which have a very close affinity with corrosion damage.

The corrosion specialist and the involved designer should primarily be concerned with achieving the optimum allowable economy in each specific case on their drawing board (see Figure 10.23). Current corrosion-control technology is usually able to offer a selection of acceptable solutions to any particular corrosion problem, although it may be difficult to select the best one without a common denominator. The selection of the optimum solution cannot thus be based only on the understanding and knowledge of corrosion technology, but the pertinent cost value must also be known. Selecting the ultimate in corrosion technology may sometimes prove the least profitable venture, and a losing proposition.

- Whilst basing the decision on a realistic appraisal of economy, a designer can distinguish which combination of material, method, technique, and system from the selected range is the best proposition, by trying to answer following questions:
- Would more expenditure on corrosion control be economically advantageous?
- Could greater savings be obtained, at the present level of expenditure, by better application of the money spent?
- Does it pay to accept a given degree of corrosion rather than to spend more money on controlling it?
- What premium on expenditure will satisfy the public requirements for safe and healthy environments?

The fullest investigation is necessary to answer these questions.

This section provides a basis guidance on the art of economic evaluation of the particulate factors of corrosion-control appreciation, without compromising the complete integrated corrosion control of the whole project. There is also special guidance regarding corrosion control that should be considered by the designer of structures, equipment, and piping systems.

10.4.1 Requirements

Where possible, and subject to availability at the time of analysis, all elements of cost should be included in the economic evaluation of corrosion control in design. These elements are as follows:

- Direct costs:
  - Direct labour (original, service, replacement; operating time for tank washing and gas freeing, fresh water rinse)
  - Direct materials (original, service, replacement)
  - Over-design (part)
  - Sub-contracts (including ex-works treatments)
  - Deterioration and preventive measures
  - Travel and transport (e.g. dock fees, etc.)
  - Contract labour
  - Consultant services
  - Sampling and testing including NDT (net data throughput) procedures
  - Pilot projects.
- Indirect costs:
  - Indirect labour
  - Indirect materials and supplies (receiving, inspection, storage, handling, etc.)
  - Over-design (part)
  - Delays
  - Safety and insurance
  - Down time (shut-down)
  - Efficiency losses
  - Product losses
  - Contamination of environment
  - Contamination and decontamination of product
  - Freight and cargo loss (due to the coating and rust scale formation)
  - Freight and cargo loss during critical period
  - Loss or gain of turnaround time (improvement of drainage in rustless tanks and vice versa)
  - Cost of potential catastrophic failure
  - Cost of potential fire
  - Repair of damage caused by corrosion to own and other properties.
- Overheads (prorated):
  - General and administrative (marketing, executive salaries, corporate expenses, etc.)
  - Rental of machinery and equipment
  - Depreciation of machinery, equipment, and facilities
  - Fringe benefits, sickness, vacation, and holidays
  - Insurance
  - Taxes, less development subsidies

- Heat and light
- Utilities
- Plant operating expenses
- Repairs and maintenance
- Research and development
- Laboratory supplies and stationery.

- Profit or loss:

  - Cost of borrowing (interest on loans)
  - Cost of capital (return on investment)
  - Recovery profits and salvage values
  - Inflation trends.

Good and comprehensive specifications are essential to any accurate economic evaluation of corrosion-control precautions. The estimator needs to know exactly what is needed from the producer/erector/assembler and applicator in order to intelligently evaluate the whole job.

Where exact instructions or specifications are not available, the contractor is going to bid and consequently furnish the product that is most economical. For a meaningful economic evaluation, the following information must be known:

- Accurate description of the job; what is to be done and what is not to be done; where the job is to be done and how long
- Avoidance of general terms of instructions; instructions to be referenced to standards or spelled out in exact technical terms and comprehensively described
- Production and application methods formulated and accurately described; machinery and tools described
- Corrosion-control systems exactly specified and the conditions of their application stated
- Safety requirements and auxiliary equipment described
- Storage and materials or product movements, workmanship, weather limitations, flow of productions and assembly, decontamination and ventilation procedures, specific instruments by trade name and number, hiring charges, inspection requirements, etc. comprehensively described

Parallel to management's anxiety at the alarming increase of the cost of construction and investment, the main concern with the economies of corrosion control in design lies in the reduction of expenditure and the increase of profits. With economics being a social science and engineering an applied science, the economic evaluation of corrosion-control contents of design serves to bridge the gap between these two human activities, to interpret the intention of relevant engineering endeavor to the management in the meaningful language of money and to temper the flight of engineering invention by the stark realities of commerce.

Any unproductive deterioration in materials and facilities by corrosion damage should be recognized as an important loss of material and human resources that could be otherwise used for a productive purpose.

The degree of corrosion control applied in the designed product is a matter of sound economics. The designer's job is to achieve the desired balance of effect for a minimum of capital outlay, maintenance, and replacement costs, cost of inconvenience and social depredations, or the potential wastage of human life. However, more expensive materials or products than absolutely necessary should not be chosen, unless it is more economical in the long run, necessary for safety, or for other important reasons.

Sometimes a timely replacement of deteriorated components may be more economical than such precautions, which require high initial expenditure or extended maintenance. The cost of remedial maintenance or the cost of "making do" with deteriorating structures and equipment should be known. Corroding components can then be replaced at a later date with new, used, or improved materials or components; the design should be adjusted accordingly.

To increase the utility of structures and equipment subject to corrosion, the designer may look at the long-term factors influencing their degree of utilization. These factors are:

- Amount of capital equipment per user
- Level of technology applied to the work
- Quality of labour force, depending on education, training, and motivation
- Skill, drive, and intent of the executive branch of the involved organization.

The groundwork of correct economic evaluation and decision-making in corrosion control rests with comprehensive recording and periodical evaluation of the cost and effectiveness of materials (including their inter-relation), systems, technologies, and personnel. This is preferably segregated for each given component, system, unit, or grouping. The whole of a given project should be covered.

Good records are better than a good memory in establishing the onset of the corrosion problem, the frequency of its occurrence, and the immediate past cost. Decisions should be reached using all information available and recorded, using the best estimates of cost, life, and other germane factors that can be obtained at the time.

Effects of previous corrosion-control precautions or procedures should be classified as to whether these are constant problems or seasonal, progressive or static. Historically documented cases of corrosion behavior of materials, structures, plant, equipment, and the methods of corrosion control should be considered with caution; the response of materials, designs and preservation systems may vary considerably in the vast variety of corrosive conditions in existence.

Where a considerable number of items important in corrosion control (e.g. corrosion failures) of a comparatively restricted and repetitive nature can be expected, electronic data processing and periodic analytical summaries may be very useful for the process of economic evaluation.

Corrosion failures, especially those associated with stress corrosion cracking, fatigue corrosion, and similar, are often, by mistake, classified under the costs of mechanical breakdowns.

In any given project, life expectancy, frequency of recurrence, etc., should be estimated and evaluated.

All estimates of life expectancy may be only an educated guess, based on a thorough study of a range of possibilities obtained by the averaging of statistical data; these do not always agree with actual experience.

The service life of existing materials, even when correlated with recorded corrosion test data, should be weighed in the light of the costs (initial cost, average yearly expense of replacement, average yearly expense of routine maintenance, average yearly expense of operating costs, average yearly expense of down time, etc.).

Information on the service life pattern of selective materials is based on the following data:

- Information on wastage limits in a given environment and in a particular location, based on the mean corrosion rate plus the standard or observed deviation
- Information on the critical thickness or strength of materials to secure the integrity of the appreciated structure or equipment
- Information on the expected material renewal periods in particular locations for various structural members or groupings

- Information on the distribution of materials amongst various structural members, or groupings by logical divisions in corrosion patterns
- Information on miscellaneous material repairs of structures and groupings
- Information on possible benefits of corrosion.

Both external and internal corrosion should be included in the estimation of the service life in progressive corrosion-rate figures.

For comparative evaluation of various technological solutions of the given corrosion problem the results of individual calculations should be converted to a common denominator, e.g. cost per day, cost per year, cost over lifetime, or any other suitable financial base.

Select the design, system, or method that will make the greatest reduction in overall operating cost and provide the prerequisite safety accounts for the first application of economics in corrosion-safe design. For estimation of corrosion-control economy, the estimator should make every effort to project the immediate past experience into the future, with the help of projection graphs, where possible.

The annual corrosion rate of steel has little or no bearing on paint selection; the main concern is with the service life of the paint system in destructive exposure and a possible occurrence of rust-creep. Neither does it affect the selection of surface preparation nor the selection of a cathodic protection system. The ultimate paint system should be restricted, for economic reasons, to aggressive areas and less expensive systems used for less destructive exposure. In the economic evaluation of painting preservation the cost of materials is not indicative on its own – the cost of labour (approximately 80%), auxiliary provisions (scaffolding, plant, ventilation, drying, lighting, and cleaning), accommodation, and transport of personnel must be included.

Surface estimating aids presented by many paint suppliers are not valid for economic evaluation of paint systems – the true surface areas form the base for estimates (texture, undulation, fasteners, flanges, etc.). For appropriate evaluation of a particular paint system, the most important factor is its maintenance cost per square meter per year, and this consideration should be coupled with the serviceability of the paint system in variable conditions (e.g. change of cargo in a ship or similar).

10.4.2 Methods of Appraisal

Having decided upon the integrated technical concept of corrosion control, the corrosion specialist must be prepared to obtain optimum economy from any conclusions and to present supporting arguments to management in terms that are readily comprehensible. Their backing must be secured, not only for the preferred corrosion control that is technically sound, but that also offers the greatest economic advantage and increases their profits. Basically, there are three possible types of decision, as follows:

- *Type 1*: Selection of optimum corrosion control for a brand new process or untested project. No money value can be consigned to corrosion control.
- *Type 2*: Clear-cut decision; concept A costs less money than concept B and has the same life expectancy, or costs the same and has a longer life – normally both lifetimes are shorter than one year.
- *Type 3*: Comparison between specific concepts of different costs and different anticipated lives, where not only the financial cost of the new project, but also the subsequent upkeep of its utility during its economic life have to be compared.

The systematic analysis of corrosion control in design is primarily concerned with the last type of financial comparison. There are several different techniques for calculating the economic appraisal of corrosion control at hand, as follows:

- Comparison of money outflow for short-term projects
- Lifetime versus cost comparison – value for money and possible cost of production losses not being considered
- Pay-out period comparison of the cost of an item of corrosion control divided by the income or savings it produces per year – taxes and time value for money not being considered
- Return on investment comparison, which is reciprocal to the pay-out period system – the results can be compared directly in terms of interest
- Annual cost comparison: the cost is multiplied by capital recovery factors for comparison of items of corrosion control with different service life, or for comparison of an item requiring major expense with another one in need of recurring expenses.
- Discounted cash flow comparison of present worth and present worth after taxes – where the value for money is also being considered.

For an overall simplified and standard approach to the economic appraisal calculations, reference is made to NACE, RP-02-72 (direct calculation of economic appraisals of corrosion-control measure, based on the method of discounted cash flow analysis.)

10.4.3 Economics Applied to Structures

The cost of structural steel design is closely related to the weight of steel used in the design; the cost of fabrication, shipping, erection, aesthetics, maintenance, and corrosion control increases with the increase of weight of steel in the structure. Amongst the other savings that accrue from lighter steel weights one may also count the occasional profit resulting from greater payloads.

Reduction in weight of structures permissible by smaller loss of strength integrity through improved corrosion control stands for direct savings in costs. The reduction of materials cost is the major consideration; fabrication cost, including processing and other costs, should also be calculated.

The trade-off between improvement of corrosion control and reduction of weight should be considered multi-laterally. Some special considerations, such as improvement of notch toughness and other precautions against stress corrosion cracking at low temperatures for cryogenic tanks, ships, and submarine design, are specifically relevant in individual cases of economic evaluation.

Corrosion control that allows planned elimination or reduction of labor motions or shop operations can reduce costs:

- Rolled shapes of any grade of steel in a structure are in most cases more economical than any built-up shapes of the same size and grade of steel.
- Rolled shapes of a higher strength may be used to replace lower strength steel shapes requiring flange plates.
- Thinner plates of higher strength steels can replace thicker plates of lower strength steels.
- Consider reduction in cost of welding and danger of stress corrosion cracking and fatigue corrosion.

The equipment used during erection of structures and the time of erection is not necessarily reduced simply by reduction of the weight of the handled components. A reduction in weight caused by improved corrosion control may accentuate the aesthetics of the structure and, by its pleasing outline, it may be inductive to a reduction in fabrication and erection costs.

Use of smaller-sized structural members, due to effective corrosion control, reduces the maintenance costs, e.g. paint and painting time. Simplification and standardization of structural members, which are conductive to improved corrosion control, also reduce the cost of maintenance and enhance maintainability. Use of corrosion-wise safer steel in structures may also provide improved economy in tension, in bending, in compression, and economy in framing and plating.

Permanent structures designed for a service life of more than five years should be protected from deterioration with the best coating system available. Other corrosion-control measures should also be considered. The cost limit in each case is individual and should not be arbitrarily dictated.

The economics of buying quality materials or techniques for treatment of new construction surfaces can be negated through incomplete specifications, poor application, or lack of inspection.

The sequence of economic rating of protective coatings for steel permanent structures is:

- Hot dip galvanizing
- Hot metal spray or zinc-rich coatings
- High built organic coatings – where zinc or other sacrificial metals cannot resist certain types of corrosion attack and as a sealer for anodic metals containing coatings in places where such metals are easily corroded.

Some economic guidelines for application of various protective coatings for standard components are as follows:

- Below 16 mm (5/8 inch) flange thickness the galvanizing is more economical – above this thickness hot metal spray, or spray and brush applied coatings are preferred.
- Galvanizing on the inside and outside of steel piping is more economic up to 30 cm (12 inches) OD – above this diameter hot metal spray, or spray and brush applied coatings are preferred.
- Galvanizing is more economical on fabricated vessels up to 1.2 m (4 ft) diameter – above this diameter hot metal spray, or brush and spray applied coatings are preferred.
- Zinc-rich paints (e.g. prefabrication primers) are more economical for plate sections of large field-fabricated tanks than other coatings.

10.4.4 Economics Applied to Equipment and Pipe Systems

The service life of materials contained in any equipment, even when correlated with corrosion test data, should be primarily weighed in the light of the actual cost. Both the damage and the cost of external and internal corrosion should be considered for evaluation of the service life of hollow equipment and pipe systems. The effect of occasional and periodic variations of internal and external environmental conditions should also be evaluated for the true extent of service life of relevant equipment.

Whilst it may not always be possible to estimate the actual money cost of equipment, it is possible to make the relevant economic decision with the help of the relative costs for comparison. This applies especially to equipment for which the price quotations vary greatly and are influenced by many factors. Thus it is more meaningful to examine the ways in which the choice of materials may affect primarily the initial cost and then future expenses.

The number of renewals forecast or necessary in the normal life-span of the equipment should be determined in the economic analysis. The degree of difficulty of the replacement of equipment or pipeline in a particular location will affect their cost. The sum of the renewals of equipment should be multiplied by the sum of labor costs that will accrue through removing and reinstalling the equipment *in situ*, and by the sum of material costs, in order to obtain a base for the calculations.

Selections providing a safe reduction in weight should be credited with the side effects of their weight reduction, e.g. lower power needed to haul given payloads, additional earning power through extra cargo capacity at the same consumption of fuel, etc.

Some factors to be considered in the economic evaluation of condensers are:

- Comparative cost of several materials
- Size and geometry of condenser to suit the variety of materials

- Comparative heat transfer factor (area of surface for a given wall thickness)
- Cleanliness factor
- Compensation for corrosion scales formed on service
- Tolerance for velocity of water to suit variety of materials, etc.

For fabricated vessels, organic coatings become more economical at a diameter of 1.2 m (4 ft) or more. The comparative throughput of transferred liquids should be used as a base for economic evaluation instead of the outside diameter of the pipes.

There is no set figure for unscheduled out-of-service time for all equipment within a utility. For example, whilst a leak in a sanitary or service piping system, although undesirable, will not stop the normal operation of a ship, a leak in a tube of a main condenser will stop the ship for cooling down, opening up, plugging the leaking tube, and closing back down.

It is more economical to galvanize both the inside and outside of pipes of up to 30 cm (12 inches) OD. Longer life expectancy can be expected from larger diameter pipes than from smaller diameter ones. Life expectancy of tubes and pipes cannot be judged on their nominal pipe thickness, the reasons being: tolerances in nominal thickness; metal removed in threading will considerably reduce the wall thickness that a pit must penetrate.

Life expectancy of pipes can also not be judged solely on the available pitting data; these tend to vary a lot. Rate of penetration is not affected by pitting only; impingement attack, erosion, etc., should all be taken into account. Pitting and preferential corrosion in the vicinity of welds make the available weight loss data of some austenitic stainless steels meaningless; note the loss in local pits or in adjacent welds.

Note, in life expectancy calculations of condenser tube materials, that the test data on a specimen do not ordinarily reflect the hot-wall effect. Economic evaluation of any equipment should not be based on any single portion of this equipment but on a balanced investigation of the whole system.

11

Fabrication and Choice of Material to Minimize Corrosion Damage

Choice of material depends on many factors, such as corrosion resistance, cost, availability, strength, appearance, and fabricability. Fabricability includes the ease of forming, welding, bending, coating, lining, and other mechanical operations. Fabrication is the process of fabricating material in a form suitable for installation and further completion of structures and equipment.

The workmanship and finish of the material should be first class in every respect and subject to the closest scrutiny by the manufacturer's inspector. Future stability of materials from a corrosion point of view depends on the design, choice of material, fabrication, inspection, installation, and final tests.

Factors affecting corrosion prevention during the service life of plants and equipment are as follows:

- Design
- Materials
- Fabrication
- Handling, storage, and erection
- Installation
- Inspection
- Operation.

11.1 Design

Where corrosion can interfere, the true functional purpose will not be achieved. Thus the designer is responsible for proper design by selective employment of qualified precautions or by optimal adjustment of the functional design.

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The designer should not concentrate purely on the functional aspects of design, to the total exclusion of other considerations, but must be aware that there are many ways in which corrosion can ruin even the best creation.

The design of a structure is frequently as important as the choice of materials of construction; it should consider mechanical and strength requirements, together with an allowance for corrosion. In all cases the mechanical design of a component should be based on the material of construction. This is important to recognize, since construction materials used for corrosion resistance vary widely in their mechanical characteristics.

There are many design rules that should be followed for the best corrosion resistance. Design in such a way as to lead corrosion out of the system instead of waiting until the equipment fails in service. It costs much less to change some lines on the drawings.

This results in close communication between designers and corrosion engineers, and all major projects include funds for utilization of corrosion engineers.

Listed below are some of the design rules that should be followed. It is helpful if the designer had a good background in corrosion, but unfortunately this is usually not the case.

- Weld rather than rivet tanks and other containers. Riveted joints provide sites for crevice corrosion.
- Design tanks and other containers for easy draining and easy cleaning. Tank bottoms should be sloped toward drain holes so that liquids cannot collect after the tank is emptied. Concentrated sulfuric acid is only negligibly corrosive toward steel. However, if a steel sulfuric acid tank is incompletely drained and the remaining liquid is exposed to the air, the acid tends to absorb moisture, resulting in dilution, and rapid attack occurs.
- Design systems for the easy replacement of components that are expected to fail rapidly in service. Frequently, pumps in chemical plants are designed so that they can be readily removed from a piping system.
- Avoid excessive mechanical stresses and stress concentrations in components exposed to corrosive mediums. Mechanical or residual stresses are one of the requirements for stress-corrosion cracking. This rule should be followed especially when using materials susceptible to stress-corrosion cracking.
- Avoid electrical contact between dissimilar metals to prevent galvanic corrosion. If possible, use similar materials throughout the entire structure, or insulate different materials from one another.
- Avoid sharp bends in piping systems when high velocities and/or solids in suspension are involved (erosion-corrosion).
- Provide thicker structures to take care of impingement effects.
- Make sure materials are properly selected.
- List complete specifications for all materials of construction and provide instructions to be sure the specs are followed all the way through to final inspection. Specify quality control procedures, if relevant.
- Be sure all relevant codes and standards are met.
- Set realistic and scheduled dates for delivery of equipment.
- Specify procedures for testing and storage of parts and equipment. For example, after hydraulic testing do not let the equipment sit full or partially full of water for any extended period of time. This could result in microbial corrosion, pitting, and stress corrosion. With regard to storage, spare stainless steel tubing shows stress-corrosion cracking when stored near the coast.
- Specify operating and maintenance procedures (i.e., scheduled shut-downs).
- Properly design against excessive vibration, not only for rotating parts but also, for example, for heat exchanger tubes.
- Provide for “blanketing” with dry air or inert gas if vessels “inhale” moist marine atmosphere while being emptied.

- Select a plant site upwind from other "polluting" plants or atmospheres, if relevant and/or feasible.
- Avoid hot spots during heat-transfer operations. Heat exchangers and other heat-transfer devices should be designed to ensure uniform temperature gradients. Uneven temperature distribution leads to local heating and high corrosion rates. Further, hot spots tend to produce stresses that may produce stress-corrosion cracking failures.
- Design to exclude air. Oxygen reduction is one of the most common cathodic reactions during corrosion, and if oxygen is eliminated, corrosion can often be reduced or prevented. In designing chemical plant equipment, particular attention should be paid to agitators, liquid inlets, and other points where air entrainment is a possibility. Exceptions to this rule are active-passive metals and alloys. Titanium and stainless steels are more resistant to acids containing dissolved air or other oxidizers.
- The most general rule for design is: avoid heterogeneity. Dissimilar metals, vapor spaces, uneven heat and stress distributions, and other differences between points in the system lead to corrosion damage. Hence, in design, attempt to make all conditions as uniform as possible throughout the entire system.

11.2 Materials

Some corrosion considerations that affect the safety of installations are specified here. Consideration should be given to allowances made for temperature and pressure effects of process reactions, and for hazards from instability of contained fluids.

The following are some general considerations that should be evaluated when selecting and applying materials:

- The possibility of exposure of the metals to fire and the melting point, degradation temperature, loss of strength at elevated temperature, and combustibility of the structural material under such exposure.
- The susceptibility to brittle failure or failure from thermal shock of the structural material when exposed to fire or to fire-fighting measures, and possible hazards from fragmentation of the material in the event of failure.
- The ability of thermal insulation to protect structure such as piping against failure under fire exposure (e.g. its stability, fire resistance, and ability to remain in place during a fire).
- The susceptibility of the piping material to crevice corrosion under backing rings, in threaded joints, in socket-welded joints, and in other stagnant, confined areas.
- The possibility of adverse electrolytic effects if the metal is subject to contact with a dissimilar metal.
- The compatibility of lubricants or sealants used on threads with the fluid service.
- The compatibility of packing, seals, and O-rings with the fluid service.
- The compatibility of materials, such as cements, solvents, solders, and brazing materials, with the fluid service.
- The chilling effect of sudden loss of pressure on highly volatile fluids as a factor in determining the lowest expected service temperature.
- The possibility of pipe support failure resulting from exposure to low temperatures (which may embrittle the supports) or high temperatures (which may weaken them).
- The compatibility of materials, including sealants, gaskets, lubricants, and insulation, used in strong oxidizer fluid service (e.g. oxygen or fluorine).

11.2.1 Specific Material Considerations: Metals

The following are some specific considerations that should be evaluated when applying certain metals in metal structures such as piping.

- Irons – cast, malleable, and high silicon (14.5%):
  - Their lack of ductility and their sensitivity to thermal and mechanical shock.
- Carbon steel, and low- and intermediate-alloy steels:
  - The possibility of embrittlement when handling alkaline or strong caustic fluids.
  - The possible conversion of carbides to graphite during long-term exposure to temperatures above 427 °C (800 °F) of carbon steels, plain nickel steel, carbon-manganese steel, manganese-vanadium steel, and carbon-silicon steel.
  - The possible conversion of carbides to graphite during long-term exposure to temperatures above 468 °C (875 °F) of carbon-molybdenum steel, manganese-molybdenum-vanadium steel, and chromium-vanadium steel.
  - The advantages of silicon-killed carbon steel (0.1% silicon minimum) for temperatures above 482 °C (900 °F).
  - The possibility of hydrogen damage to piping material when exposed (under certain temperature and pressure conditions) to hydrogen or aqueous acid solutions.
  - The possibility of stress corrosion cracking when exposed to wet hydrogen sulfide (a maximum hardness limit is usually specified; see API RP 942), and the further possibility of deterioration (sulfidation) in the presence of hydrogen sulfide at elevated temperatures.
  - The importance of limiting maximum hardness of metals in applications subject to stress corrosion.
- High-alloy (stainless) steels:
  - The possibility of stress corrosion cracking of austenitic stainless steels exposed to media such as chlorides and other halides, either internally or externally; the latter can result from improper selection or application of thermal insulation.
  - The susceptibility to intergranular corrosion of austenitic stainless steels after sufficient exposure to temperatures between 427 °C and 871 °C (800 °F and 1600 °F) unless stabilized or low-carbon grades are used.
  - The susceptibility to intercrystalline attack of austenitic stainless steels on contact with zinc or lead above their melting points, or with many lead and zinc compounds at similarly elevated temperatures.
  - The brittleness of ferritic stainless steels at room temperature after service at temperatures above 371 °C (700 °F).
  - The susceptibility to grain boundary attack of nickel-based alloys containing chromium at temperatures above 593 °C (1100 °F) under reducing conditions and above 760 °C (1400 °F) under oxidizing conditions.
  - The possibility of stress corrosion cracking of nickel-copper alloy (70Ni-30Cu) in hydrofluoric acid vapor if the alloy is highly stressed or contains residual stresses from forming or welding.
- Aluminum and aluminum alloys:
  - The compatibility with aluminum of thread compounds used in aluminum threaded joints to prevent seizing and galling.
  - The possibility of corrosion from concrete, mortar, lime, plaster, or other alkaline materials used in buildings or structures.

  - The susceptibility of Alloy Nos. 5083, 5086, 5154, and 5456 to exfoliation or intergranular attack; and the upper temperature limit of 66 °C (150 °F) to avoid such deterioration.

- Copper and copper alloys:
  - The possibility of dezincification of brass alloys.
  - The susceptibility to stress-corrosion cracking of copper-based alloys exposed to fluids such as ammonia or ammonium compounds.
  - The possibility of unstable acetylide formation when exposed to acetylene.
- Titanium and titanium alloys:
  - The possibility of deterioration of titanium and its alloys above 316 °C (600 °F).
- Zirconium and zirconium alloys:
  - The possibility of deterioration of zirconium and zirconium alloys above 316 °C (600 °F).
- Tantalum:
  - Above 299 °C (570 °F), the possibility of reactivity of tantalum with all gases except inert gases. Below 299 °C the possibility of embrittlement of tantalum by nascent (monatomic) hydrogen (but not molecular hydrogen). Nascent hydrogen is produced by galvanic action, or as a product of corrosion by certain chemicals.
- Metals with enhanced properties:
  - The possible loss of strength, in a material whose properties have been enhanced by heat treatment, during long continued exposure to temperatures above its tempering temperature.

11.2.2 Material Considerations: Non-metals

The following are some considerations to be evaluated when applying non-metals in structures such as piping:

- Static charges: because of the possibility of producing hazardous electrostatic charges in non-metallic piping and metallic piping lined with non-metals, consideration should be given to grounding the metallic components of such systems conveying non-conductive fluids.
- Thermoplastics: if thermoplastic piping is used above ground for compressed air or other compressed gases, special precautions should be observed. In determining the needed safeguarding for such services, the energetics and the specific failure mechanism need to be evaluated. Encasing the plastic piping in shatter-resistant material may be considered.
- Borosilicate glass: take into account its lack of ductility and its sensitivity to thermal and mechanical shock.

11.3 Fabrication

- The concerned fabricator should follow the fabrication procedures introduced by the designer precisely, and use the specified methods and materials prescribed.
- In addition, the contractor and fabricator should give consideration to all factors affecting fabrication that in turn facilitate improvement of the resistance of equipment and structures to corrosion.
- When an engineer is responsible for the whole construction, they are also responsible for the performance of first-class fabrication.

- Due consideration should be given to special treatment required for different materials to improve resistance to corrosion, e.g. special welding techniques, stress relieving, blast peening, metallizing, sealing of welds, etc.; also to any fabrication or assembly methods that would aggravate any tendency of the material to corrosion failure.
- With approval of the designer, alloys in as highly alloyed a condition as necessary should be used when the cost of fabrication is higher than the cost of the basic material. The proportional cost of material for multi-shaped or complicated components is much less than for simple ones.
- Distribute stress with the metals' anisotropic characteristics in mind:
  - Either avoid exposing traverse planes or protect them.
  - Avoid or relieve residual stress from quenching and fitting.
  - Select fabrication with special attention to avoid consequence, of high localized stress pattern.
  - Select fabrication, machining, and assembly operations imparting minimum residual stresses, fillets should be streamlined if possible.
- Protective coatings should be applied after all punching, drilling, machining, forming, and fabrication has been completed; paint finishing systems, if required, may also be applied after metal deposition or over chemical film treatment.
- The workmanship and finish should be first class in every respect and subject to the closest scrutiny by the manufacturer's inspector, whether or not the purchaser waives any part of the inspection.
- When material requires straightening, the work should be done by pressing or another non-injurious method prior to any layout or shaping. Heating or hammering is not permissible unless the material is heated to a forging temperature.

Factors affecting fabrication can be classified as follows:

- Design and materials, both of which have been described earlier
- Welding
- Welding and joining
- Bending and forming
- Brazing and soldering
- Heat treatment
- Preheating
- Coating and lining.

11.3.1 Welding

11.3.1.1 Corrosion of Weldments

It is not unusual to find that, although the wrought form of a metal or alloy is resistant to corrosion in a particular environment, the welded counterpart is not. Further, welds can be made with the addition of filler metal or can be made autogenously (without filler metal). However, there are also many instances in which the weld exhibits corrosion resistance superior to that of the unwelded base metal, as well as times when it behaves in an erratic manner, displaying both resistance and susceptibility to corrosive attack.

Corrosion failures of welds occur in spite of the fact that the appropriate base metal and filler metal have been selected, industry codes and standards have been followed, and welds have been deposited that possess full penetration and have the proper shape and contour. It is sometimes difficult to determine why welds corrode; however, one or more of the following factors are often implicated:

- Weldment design
- Fabrication technique
- Welding practice
- Welding sequence
- Moisture contamination
- Organic or inorganic chemical species
- Oxide film and scale
- Weld slag and spatter
- Incomplete weld penetration or fusion
- Porosity
- Cracks (crevices)
- High residual stresses
- Improper choice of filler metal
- Final surface finish.

ASME Section IX and API 1104 discuss the welding of pressure vessels and line pipe, including the requirements for qualifying welding procedures, welders, and the quality level of the production weldments. These standards also identify the variables that dictate when different procedures are required to cover material thickness, material chemistry, joint design, welding position, and thermal treatments. If weldments are to be used in H_2S environments, such factors as additional hardness testing, the type of welding electrode, and the wire/flux combination used should be considered.

The American Petroleum Institute and the National Association of Corrosion Engineers publish documents that indicate whether weldments made with certain wire/flux combinations have experienced failure in H_2S environments under conditions in which failures were unexpected. Weldments with high manganese and silicon contents have been shown to be very susceptible to sulfide stress cracking at levels of hardness at or below 22 HRC, even after thermal treatments.

If temperature is an environmental consideration, the designer should be aware that the ability of materials and weldments to withstand sudden impact loading decreases significantly with temperature. Materials and weldments that have ductile characteristics at room temperature (20 °C, or 70 °F) may behave in a brittle manner when exposed to lower temperatures.

In addition to the typical mechanical-property testing of materials and weldments, impact testing is required to ensure that the product is properly designed for the anticipated operating temperatures. Standards from ASTM, ASME, and others address these design requirements and generally specify materials that have Charpy V-notch impact test requirements added to the normal mechanical property tests.

In the case of weldments, Charpy V-notch impact testing of the base metal, the heat-affected zone, and the weld metal is also required to ensure that the weldment will function satisfactorily at the design temperature. Welding must be performed with care to ensure that the completed weldment is produced in accordance with standard procedures.

API 14D establishes requirements for well-head surface safety valves (SSV valves), underwater safety valves (USV valves), and their actuators (SSV/USV actuators). The requirements include design, materials quality, performance testing, and functional testing.

Equipment manufactured to this specification is primarily intended for service in outer continental shelf (OCS) waters contiguous to the United States. The equipment is identified with the API 14D monogram.

It is also eligible for the OCS monogram when manufactured under a quality program conforming to ANSI/ASME-SPPE-1 specifications. The federal government has mandated that all such equipment installed in federal OCS waters have both monograms.

The ANSI/ASME-SPP-1 standards establish requirements for quality programs, accreditation of quality programs, and reporting of malfunctions and failures. Manufacturers conforming to these standards are authorized by ASME to apply the OCS monogram to SSVs (valves and actuators).

11.3.1.2 Metallurgical Factors

The cycle of heating and cooling that occurs during the welding process affects the micro-structure and surface composition of welds and adjacent base metal. Consequently, the corrosion resistance of autogenous welds and welds made with matching filler metal may be inferior to that of properly annealed base metal because of:

- Microsegregation
- Precipitation of secondary phases
- Formation of unmixed zones
- Recrystallization and grain growth in the weld heat-affected zone (HAZ)
- Volatilization of alloying elements from the molten weld pool
- Contamination of the solidifying weld pool.

Corrosion resistance can usually be maintained in the welded condition by balancing alloy compositions to inhibit certain precipitation reactions, by shielding molten and hot metal surfaces from reactive gases in the weld environment, by removing chromium-enriched oxides and chromium-depleted base metal from thermally discolored (heat-tinted) surfaces, and by choosing the proper welding parameters.

11.3.1.3 Weld Solidification

During the welding process, a number of important changes occur that can significantly affect the corrosion behavior of the weldment. Heat input and welder technique obviously play important roles. The way in which the weld solidifies is equally important to understanding how weldments may behave in corrosive environments.

A metallographic study has shown that welds solidify into various regions, as illustrated in Figure 11.1. The composite region, or weld nugget, consists of essentially filler metal that has been

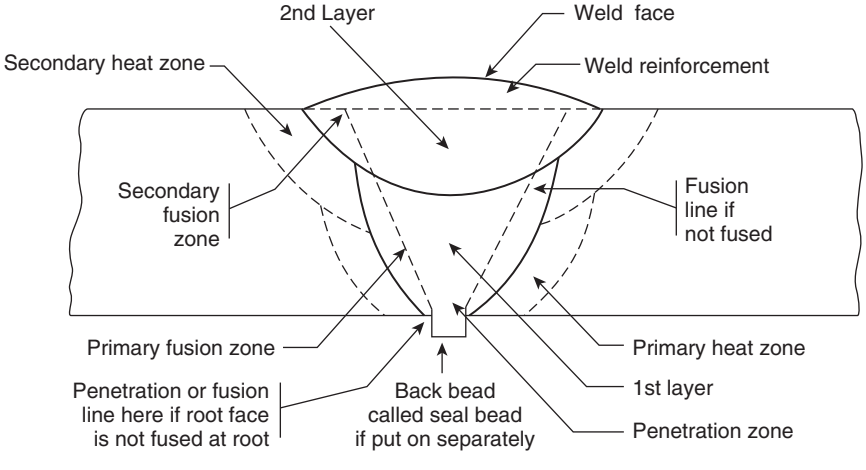


Figure 11.1 *Schematic of a weld cross section.*

diluted with material melted from the surrounding base metal. Next to the composite region is the unmixed zone, a zone of base metal that melted and solidified during welding without experiencing mechanical mixing with the filler metal.

The weld interface is the surface bounding the region within which complete melting was experienced during welding, and is evidenced by the presence of a cast structure. Beyond the weld interface is the partially melted zone, which is a region of the base metal within which the proportion melted ranges from 0 to 100%. Lastly, the true heat-affected zone (HAZ) is that portion of the base metal within which microstructural change has occurred in the absence of melting.

Although the various regions of a weldment shown in Figure 11.1 are for a single-pass weld, similar solidification patterns and compositional differences can be expected to occur in underlying weld beads during multi-pass applications.

11.3.1.4 Corrosion of Carbon Steel Weldments

The corrosion behavior of carbon steel weldments is dependent on a number of factors. Consideration must be given to the compositional effects of the base metal and welding consumable and to the different welding processes used. Because carbon steels undergo metallurgical transformations across the weld and HAZ, micro-structures and morphologies become important.

A wide range of micro-structures can be developed, based on cooling rates, and these micro-structures are dependent on energy input, preheat, metal thickness (heat-sink effects), weld bead size, and reheating effects due to multi-pass welding.

As a result of their different chemical compositions and weld inclusions (oxides and sulfides), weld metal micro-structures are usually significantly different from those of the HAZ and base metal. Similarly, corrosion behavior can also vary.

In addition, hardness levels will be lowest for high heat inputs, such as those produced by submerged arc weldments, and will be highest for low-energy weldments (with faster cooling rates) made by shielded metal arc processes. Depending on the welding conditions, weld metal micro-structures generally tend to be fine grained with basic flux, and somewhat coarser with acid or rutile (TiO_2) flux compositions.

During welding, the base metal, HAZ, and underlying weld passes experience stresses due to thermal expansion and contraction. Upon solidification, rather high levels of residual stress remain as a result of weld shrinkage. Stress concentration effects as a result of geometrical discontinuities, such as weld reinforcement and lack of full weld penetration (dangerous because of the likelihood of crevice corrosion and the possibility of fatigue cracking), are also important because of the possibility of SCC.

Achieving full weld penetration, minimizing excessive weld reinforcement through control of the welding process or technique, and grinding (a costly method) can be effective in minimizing these geometric effects. A stress-relieving heat treatment is effective in reducing internal weld shrinkage stress and metal hardness to safe levels in most cases.

11.3.1.5 Preferential Heat-Affected Zone Corrosion

An example of preferential weld corrosion in the HAZ of a weldment is shown in Figure 11.2. This phenomenon has been observed in a wide range of aqueous environments, the common link being that the environments are fairly high in conductivity, while attack has usually, but not invariably, occurred at pH values below about 7 to 8.

The reasons for localized weldment attack have not been fully defined. There is clearly a microstructural dependence, and studies on HAZs show corrosion to be appreciably more severe when the material composition and welding are such that hardened structures are formed.

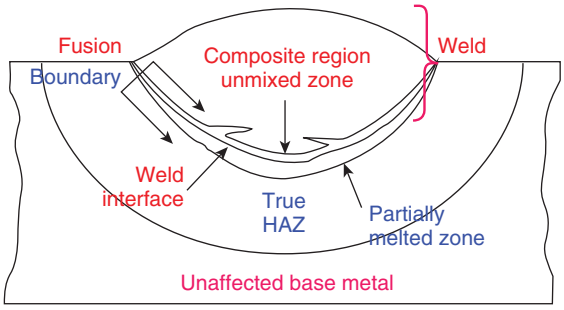


Figure 11.2 *A single pass C-Mn steel weldment showing HAZ.*

It has been known for many years that hardened steel may corrode more rapidly in acid conditions than fully tempered material, apparently because local micro-cathodes on the metal surface stimulate the cathodic hydrogen evolution reaction.

On this basis, water treatments ensuring alkaline conditions should be less likely to induce HAZ corrosion, but even at pH values near 8, hydrogen ion (H^+) reduction can account for about 20% of the total corrosion current; pH values substantially above this level would be needed to suppress the effect completely.

Figure 11.3 shows optical micrographs of the base steel and simulated HAZs.

11.3.1.6 Preferential Weld Corrosion

It is probable that similar microstructural considerations also apply to the preferential corrosion of weld metal, but in this case, the situation is further complicated by the presence of de-oxidation products, their type and number depending largely on the flux system employed.

Consumable type plays a major role in determining weld metal corrosion rate, and the highest rates of metal loss are normally associated with shielded metal arc electrodes using a basic coating. In seawater, for example, the corrosion rate for a weld made using a basic-coated consumable may be three times as high as for weld metal from a rutile-coated consumable.

Fewer data are available for submerged arc weld metals, but it would appear that they are intermediate between basic and rutile shielded metal arc electrodes and that a corrosion rate above that of the base steel can be expected.

11.3.1.7 Galvanic Corrosion

Galvanic corrosion effects have also been observed and have caused unexpected failure of piping tankage and pressure vessels where the welds are anodic to the base metal. The following examples illustrate the point.

In one case, premature weld failures were experienced in a 102 mm (4 inch) ASTM A53 pipe that was used to transfer a mixture of chlorinated hydrocarbons and water. During construction, the pipeline was fabricated with E7010-Al welding electrodes (see Table 11.1 for the composition limits for all materials discussed in these examples).

Initial weld failures and subsequent tests showed the following welding electrodes to be anodic to the A53 Grade B base metal: E7010-Al, E6010, E6013, E7010-G, and E8018-C2. Two nickel-based electrodes, Inco-Weld A (AWS A5,11, Class ENiCrFe-2) and Incoloy welding electrode 135 were tested; they were found to be cathodic to the base metal and to prevent rapid weld corrosion. The corrosion rates of these various galvanic couples are listed in Table 11.2.

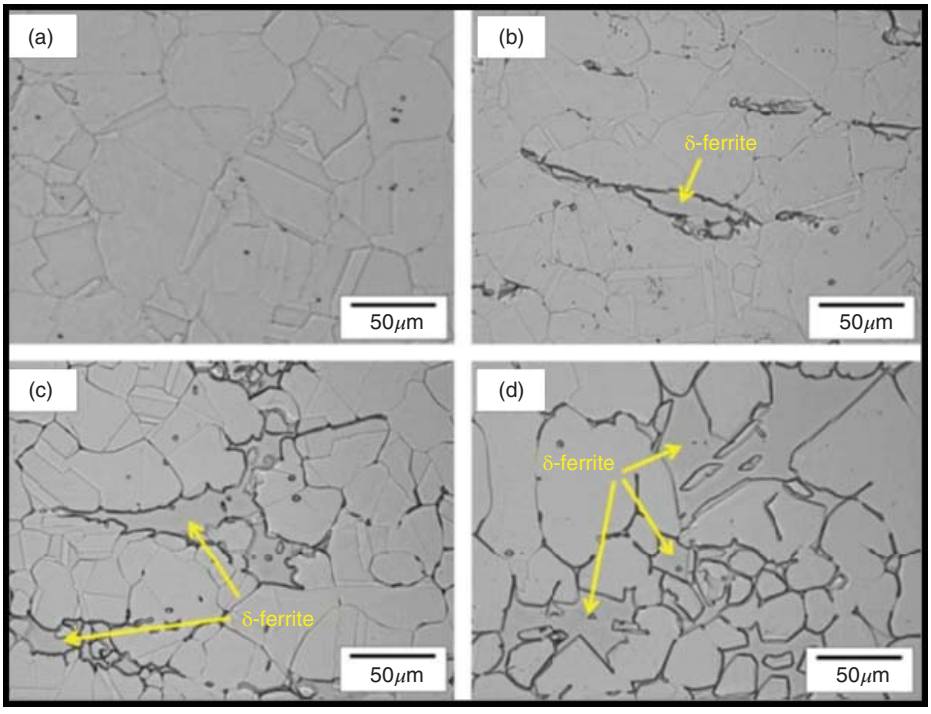


Figure 11.3 *Optical micrographs of the base steel and simulated HAZs: (a) base metal, (b) HAZ 1 with 1200°C peak temperture, (c) HAZ 2 with 1300°C peak temperature and (d) HAZ 3 with 1350°C peak temperature, respectively. (Reprinted from J. Moon, Heon-Young Ha, Tae-Ho Lee, 2013, with permission from Elsevier.)*

Another example is the failure of low-carbon steel welds in seawater service at 25 °C (75 °F). Fabrications involving ASTM A285, Grade C, plate-welded with E6013 electrodes usually start to fail in the weld after 6 to 18 months in seawater service at this temperature. Welds made with E7010 electrodes do not fail. Tests were conducted in seawater at 50 °C (120 °F) using A285, Grade C, plate-welded with E6010, E7010-Al, and E7010-G.

It was determined that E7010- Al was the best electrode to use in seawater and that E6010 and E7010-G were not acceptable (although they were much better than E6013), because they were both anodic to the base metal. A zero resistance ammeter was used to determine whether the electrodes were anodic or cathodic in behavior.

In another case, welds made from E7010-Al electrodes to join ASTM A285, Grade C, base metal were found to be anodic to the base metal when exposed to raw brine, an alkaline-chloride (pH > 7) stream, and raw river water at 50 °C (120 °F). When E7010-G was exposed to the same environment, it was anodic to the base metal in raw brine and raw river water, and was cathodic to ASTM A285, Grade C, in the alkaline-chloride stream. When the base metal was changed to ASTM A53, Grade B, and A106, Grade B, it was found that E7010-Al weld metal was cathodic to both when exposed to raw brine at 50 °C (120 °F).

Finally, routine inspection of a column in which a mixture of hydrocarbons was water washed at 90 °C (195 °F) revealed that E7016 welds used in the original fabrication were corroding more rapidly than the ASTM A285, Grade C, base metal. Corroded welds were ground to sound metal, and E7010-Al was used to replace the metal that was removed.

Table 11.1 *Compositions of carbon steel base metals and some filler metals subject to galvanic corrosion*

Metal	Composition, %						
	C	Mn	Si	Cr	Ni	Fe	Others
Base metals							
ASTM A53, Grade B	0.3	1.2	–	–	–	Balance	–
ASTM A285, Grade C	0.22	0.9	–	–	–	Balance	–
Filler Metals							
E6010	No specific chemical limits						
E6013							
E7010-Al	0.12	0.6	0.4	–	–	Balance	0.4–0.65Mo
E7010-G	–	1*	0.8*	0.3*	0.5*	Balance	0.2Mo, 0.1V
E7016	–	1.25**	0.9	0.2**	0.3**	Balance	0.3Mo, 0.08V**
E7018	–	1.6***	0.75	0.2***	0.3***	Balance	0.3Mo, 0.08V***
E8018-C2	0.12	1.2	0.8	–	2–2.75	Balance	1–3.5Mo, 0.5Cu
ENiCrFe-2 (Inco Weld A)	0.10	1–3.5	1	13–17	Balance	12	0.5–3 (Nb + Ta)
Incoloy welding electrode 135	0.08	1.25–2.5	0.75	26.5–30.5	35–40	Balance	2.75–4.5Mo, 1–2.5Cu

*The weld deposit must contain only the minimum of one of these elements.
**The total of these elements should not exceed 1.50%.
***The total of these elements should not exceed 1.75%.

Table 11.2 *Corrosion rates of galvanic couples of ASTM A53, Grade B, base metal, and various filler metals in a mixture of chlorinated hydrocarbons and water (the areas of the base metal and the deposited weld metal were equal)*

Galvanic couple	Corrosion rate	
	mm/yr	mils/yr
Base metal	0.4	15
E6010	0.9	35
Base metal	0.18	7
E6013	0.9	35
Base metal	1.3	50
E7010-Al	4.3	169
Base metal	1.7	68
E7010-G	2.8	112
Base metal	0.36	14
E8018-C2	1.7	66
Base metal	0.48	19
Inco Weld A	0.013	0.5
Base metal	0.36	14
Incoloy welding electrode 135	< 0.0025	< 0.1

Table 11.3 *Corrosion rates of galvanic couples of ASTM A285, Grade C, base metal, and various filler metals at 90 °C (195 °F) in water used to wash a hydrocarbon stream*

Galvanic couple	Corrosion rate	
	mm/yr	mils/yr
Base metal	0.69	27
E7010-Al	0.81	32
Base metal	0.46	18
E7016	0.84	33
Base metal	1.3	50
E7018	1.2	48
Base metal	2.2	85
E8018-C2	1.04	41

About three years later, during another routine inspection, it was discovered that the E7010-Al welds were being selectively attacked. Tests were conducted that showed E7010-Al and E7016 weld metals to be anodic to A285, Grade C, while E7018 and E8018-C2 would be cathodic. Corrosion rates of these various galvanic couples are given in Table 11.3.

These examples demonstrate the necessity for testing each galvanic couple in the environment for which it is intended. Higher-alloy filler metals can sometimes be used to advantage to prevent rapid preferential weld corrosion.

11.3.1.8 Stress-Corrosion Cracking

There is no doubt that residual welding stresses can cause SCC in environments in which such failure represents a hazard. This is the case for failure by both active path and hydrogen embrittlement mechanisms, and in the latter case, failure may be especially likely at low heat input welds because of the enhanced susceptibility of the hardened structures inevitably formed.

Most SCC studies of welds in carbon and carbon-manganese steels have evaluated resistance to hydrogen-induced SCC, especially under sour (H_2S) conditions prevalent to the oil and gas industry. The situation regarding active path cracking is less clear, but there are few, if any, cases in which SCC resistance increases at higher strength levels. On this basis, it is probable that soft, transformed micro-structures around welds are preferable.

Carbon and low-alloy steels are also known to fail by SCC when exposed to solutions containing nitrates (NO_3^-). Refrigeration systems using a 30% magnesium nitrate ($Mg(NO_3)_2$) brine solution, for example, are commonly contained in carbon steel. In this case, pH adjustment is important, as is temperature. Failures in the HAZ due to SCC have been reported when brine temperatures have exceeded 30 °C (90 °F) during shut-down periods.

To avoid these failures, carbon steel is being replaced with Type 304L stainless. Others have stress-relieved welded carbon steel systems and have operated successfully, although elevated-temperature excursions are discouraged.

More recently, it has been shown that cracking can occur under certain conditions in carbon dioxide (CO_2)-containing environments, sometimes with spectacular and catastrophic results. Processes in the oil, gas, and chemical industries require removal of CO_2 from process streams by a variety of absorbents. In most cases, process equipment is fabricated from plain carbon steel.

11.3.1.9 Corrosion of Austenitic Stainless Steel Weldments

The corrosion problems commonly associated with welding of austenitic stainless steels are related to precipitation effects and chemical segregation. These problems can be eliminated or minimized through control of base metal metallurgy, control of the welding practice, and selection of the proper filler metal.

11.3.1.10 Pitting Corrosion

Under moderately oxidizing conditions, such as a bleach plant, weld metal austenite may suffer preferential pitting in alloy-depleted regions. This attack is independent of any weld metal precipitation and is a consequence of microsegregation or coring in weld metal dendrites. Preferential pitting is more likely in autogenous (no filler) gas tungsten arc (GTA) welds, in 4 to 6% Mo alloys (Table 11.4), when the recommended filler metal has the same composition as the base metal, and when higher heat

Table 11.4 *Amounts of principal alloying elements in stainless steels tested for pitting resistance*

Alloy	Composition, %			
	Cr	Ni	Mo	N
Base metals				
Type 316L	16	13	2.8	–
Type 317L	18	14	3.2	–
34L	17	1	54.3	–
34LN	18	14	4.7	–
1.4439	18	14	4.3	0.13
Nitronic 50	21	14	2.2	0.2
20Cb-3	20	33	2.4	–
Alloy 904L	20	25	4.2	–
2RK65	20	25	4.5	–
JS700	21	25	4.5	–
19/25LC	20	25	4.8	–
AL-6X	20	24	6.6	–
254SMO	20	18	6.1	–
19/25HMO	21	25	5.9	0.2
Filler metals				
Type 316L	19	12	2.3	–
Type 317L	19	13	3.8	–
309MoL 23	14	2.5	–	–
Batox Cu	19	24	4.6	–
254SLX 20	24	5	–	–
SP-281 20	25	4.6	–	–
Jungo 4500	20	26	4.4	–
Nicro 31/27	28	30	3.5	–
Thermanit 30/40E	28	35	3.4	–
SAN 27.31.4.LCuR	27	31	3.5	–
Incoloy Alloy 135	27	31	3.5	–
Hastelloy Alloy G	22	38	3.7	–
P12	21	61	8.6	–
Inconel Alloy 112	21	61	8.7	–
Hastelloy Alloy C-276	15	58	15.4	–

Table 11.5 *Filler metals with pitting resistance close to or better than that of the corresponding base metals*

Base metal	Filler metals
Type 316L	316L, 317L, 309MoL
Type 317	317L, 309MoL
Alloy 904	Sandvik 27.31.4.LCuR; Thermanit 30/40 E, Nicro 31/27;Fox CN 20 25 M, IN-112, Avesta P12, Hastelloy Alloy C-276
Avesta 254 SMO	Avesta P12, IN-112, Hastelloy Alloy C-276

input welding leaves a coarse micro-structure with surface-lying dendrites. Such a micro-structure is avoided by use of a suitably alloyed filler metal.

Filler metals with pitting resistance close to or better than that of the corresponding base metals are included in Table 11.5

Even when suitable fillers are used, preferential pitting attack can still occur in an unmixed zone of weld metal. High heat input welding can leave bands of melted base metal close to the fusion line. The effect of these bands on corrosion resistance can be minimized by welding techniques that bury unmixed zones beneath the surface of the weldment.

When the wrong filler metal is used, pitting corrosion can readily occur in some environments, for example when the Type 316L base metal is welded with a lower-alloy filler metal (Type 308L).

11.3.1.11 Crevice Corrosion

In order for crevice corrosion to develop we must have the following conditions:

- An area of the part/component/assembly that has access to oxygen
- An area of the part/component that is deprived of oxygen
- An electrolyte that develops in the oxygen-deprived area; this typically occurs due to water or stagnant solution seeping into crevices in the steep part/component/assembly.

Figure 11.4 illustrates a typical way in which crevice corrosion is formed at welding joint.

Figure 11.5 shows the crevice corrosion that occurred beneath the seal (white circle on the left side of the picture). The part/component on the right is known as a flange.

Defects such as residual welding flux and micro-fissures create weld metal crevices that are easily corroded, particularly in chloride-containing environments. Some flux formulations on coated shielded metal arc or stick electrodes produce easily detached slags, and others give slags that are difficult to remove completely, even after grit-blasting.

Slags from rutile (titania-based) coatings are easily detached and have a good bead shape. In contrast, slags from basic-coated electrodes for out-of-position welding can be difficult to remove; small particles of slag may remain on the surface, providing an easy initiation site for crevice attack.

Micro-fissures or their larger counterparts, hot cracks, also provide easy initiation sites for crevice attack, which will drastically reduce the corrosion resistance of a weldment in a bleach plant.

Micro-fissures are caused by thermal contraction stresses during weld solidification and are a problem that plagues austenitic stainless steel fabrications. These weld metal cracks are more likely to form when phosphorus and sulfur levels are higher (that is, more than 0.015% P and 0.015% S), with high heat input welding, and in austenitic weld metal in which the α-ferrite content is low ($< 3\%$).

Small-scale micro-fissures are often invisible to the naked eye, and their existence can readily explain the unexpectedly poor pitting performance of one of a group of weldments made with filler metals of apparently similar general composition.

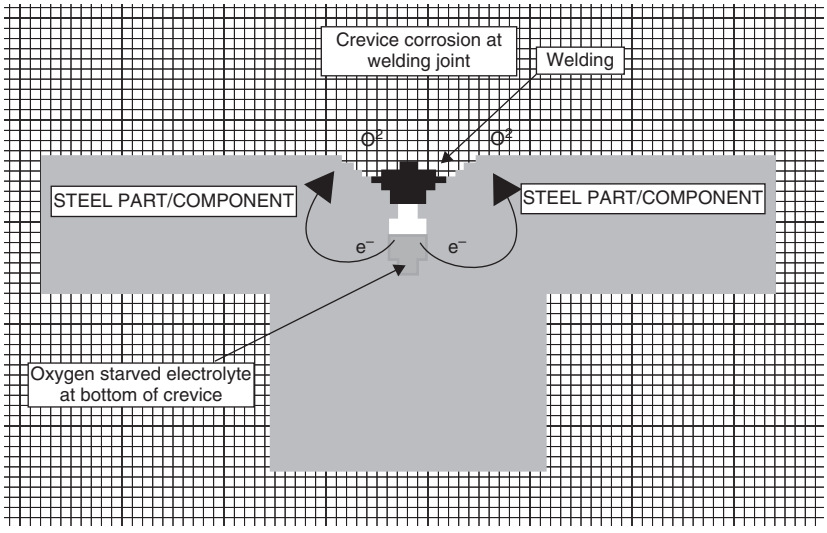


Figure 11.4 *Crevice corrosion at a welding joint. (Reproduced with permission from Daubert Cromwell.)*



Figure 11.5 *An example of crevice corrosion. (Reproduced with permission from Analog © Luis Orozco.)*

The micro-fissure provides a crevice that is easily corroded because stainless alloys are more susceptible to crevice corrosion than to pitting. However, micro-fissure crevice corrosion is often mistakenly interpreted as self-initiated pitting.

Crevice corrosion sites can also occur at the beginning or end of weld passes, between weld passes, or under weld spatter areas. Weld spatter is most troublesome when it is loose or poorly adherent.

Micro-fissure corrosion in austenitic stainless steel weldments containing 4 to 6% Mo is best avoided with the nickel-based Inconel 625, Inconel 112, or Avesta P12 filler metals, which are very resistant to crevice attack. Some stainless electrodes are suitable for welding 4% Mo steels, but they should be selected with low phosphorus and sulfur to avoid micro-fissure problems.

Hot tap water is not thought to be particularly aggressive; however, it can damage a weld that contains a lack-of-fusion defect in the presence of chlorides. In this case, the base metal is Type 304 stainless steel, and the weld metal Type 308.

11.3.1.12 Carbide Precipitation in the HAZ

The best known weld-related corrosion problem in stainless steels is weld decay (sensitization) caused by carbide precipitation in the weld HAZ.

Sensitization occurs in a zone subject to a critical thermal cycle in which chromium-rich carbides precipitate and in which chromium diffusion is much slower than that of carbon. The carbides are precipitated on grain boundaries that are consequently flanked by a thin chromium-depleted layer. This sensitized micro-structure is much less corrosion resistant, because the chromium-depleted layer and the precipitate can be subject to preferential attack. Sensitization can be avoided by the use of low-carbon grades such as Type 316L (0.03% C max.) in place of sensitization-susceptible Type 316 (0.08% C max.).

It is more common to use 0.05% C (max.) steels, which are still reasonably resistant to sensitization, particularly if they contain molybdenum and nitrogen; these elements appear to raise the tolerable level of carbon and/or heat input. However, low-carbon stainless steels carry a small cost premium; therefore, they are not universally specified.

At higher solution temperatures, sensitized Type 304 and Type 316 are particularly susceptible to SCC – whether caused by chlorides, sulfur compounds, or caustic. In many cases cracking occurs after HCl acid cleaning.

Although the initial crack path may be intergranular, subsequent propagation can have the characteristic branched appearance of transgranular chloride SCC. Intergranular SCC caused by sulfur compounds can also occur during the acid cleaning of sensitized stainless steels.

11.3.1.13 Corrosion Associated with Postweld Cleaning

Postweld cleaning is often specified to remove the heat-tinted metal formed during welding. Recent work has shown that cleaning by stainless steel wire brushing can lower the corrosion resistance of a stainless steel weldment.

This is a particular problem in applications in which the base metal has marginal corrosion resistance. The effect may be caused by inadequate heat-tint removal, by the use of lower-alloy stainless steel brushes such as Type 410 or 304, or by the redeposition of abraded metal or oxides.

Any cleaning method may be impaired by contamination or by lack of control. Results of a study in bleach plants suggest that pickling and glass bead blasting can be more effective than stainless wire brushing and that brushing is more difficult to perform effectively in this case.

11.3.1.14 Corrosion associated with weld backing rings

Backing rings are sometimes used when welding pipe. In corrosion applications, it is important that the backing ring insert be consumed during the welding process to avoid a crevice. The best solution to this problem was to eliminate the crevices, that is, not to use backing rings.

11.3.1.15 Corrosion of Ferritic Stainless Steel Weldments

Conventional 400 series ferritic stainless steels such as AISI Types 430,434, and 446 are susceptible to intergranular corrosion and to embrittlement in the as-welded condition. Corrosion in the weld area generally encompasses both the weld metal and weld HAZ. Early attempts to avoid some of these



Figure 11.6 *As-welded Type 430 stainless steel saturator tank used in the manufacture of carbonated water that failed after two months of service. The tank was shielded metal arc welded using Type 308 stainless steel filler metal. (Reproduced with permission from Daubert Cromwell.)*

problems involved the use of austenitic stainless steel filler metals; however, failure by corrosion of the HAZ usually occurred even when exposure was to rather mild media for relatively short periods of time.

Figure 11.6 shows an example of a saturator tank used to manufacture carbonated water at room temperature that failed by leakage through the weld HAZ of the base metal after being in service for only two months. This vessel, fabricated by welding with a Type 308 stainless steel welding electrode, was placed in service in the as-welded condition.

To overcome some of the earlier difficulties and to improve weldability, several of the standard grade ferritic stainless steels have been modified. For example, Type 405, containing nominally 11% Cr, is made with lower carbon and a small aluminum addition of 0.20% to restrict the formation of austenite at high temperature so that hardening is reduced during welding.

For maximum ductility and corrosion resistance, however, postweld annealing is necessary. Recommendations for welding include either a Type 430 or a Type 309 filler metal, the latter being used where increased weld ductility is desired.

11.3.1.16 A New Generation of Ferritic Stainless Steels

In the late 1960s and early 1970s, researchers recognized that the high chromium–molybdenum–iron ferritic stainless steels possessed a desirable combination of good mechanical properties and resistance to general corrosion, pitting, and SCC. These properties made them attractive alternatives to the austenitic stainless steels commonly plagued by chloride SCC.

Table 11.6 *Typical compositions of some ferritic stainless steels*

Alloy	Composition, %						
	C (max.)	Cr	Fe	Mo	N	Ni	Other
Standard grades (AISI 400 series)							
Type 405	0.08	13	Balance	–	–	–	0.2Al
Type 430	0.12	17	Balance	–	–	–	–
Type 430Ti	0.10	17	Balance	–	–	–	Ti6 × C min.
Type 434	0.12	17	Balance	0.75–1.25	–	–	–
Type 446	0.2	25	Balance	–	–	–	–
Intermediate purity grades							
Ti 26-1	0.02	26	Balance	1	0.025	0.25	0.5Ti
AISI Type 444	0.02	18	Balance	2	0.02	0.4	0.5Ti
Sea-Cure	0.02	27.5	Balance	3.4	0.025	1.7	0.5Ti
Monit	0.025	25	Balance	4	0.025	4	0.4Ti
Ultrahigh purity grades							
E-Brite 26-1	0.002	26	Balance	1	0.01	0.1	0.1 Nb
AL 29-4-2	0.005	29	Balance	4	0.01	2	–
SHOMAC 26-4	0.003	26	Balance	4	0.005	–	–
SHOMAC 30-2	0.003	30	Balance	2	0.007	0.18	–
YUS 190L	0.004	19	Balance	2	0.0085	–	0.15 Nb

It was reasoned that by controlling the interstitial element (carbon, oxygen, and nitrogen) content of these new ferritic alloys, either by ultrahigh purity or by stabilization, the formation of martensite (as well as the need for preheat and postweld heat treatment) could be eliminated, with the result that the welds would be corrosion resistant, tough, and ductile in the as-welded condition. To achieve these results, electron beam vacuum refining, vacuum and argon–oxygen decarburization, and vacuum induction melting processes were used. From this beginning, two basic ferritic alloy systems evolved:

- Ultrahigh purity: the (C + N) interstitial content is less than 150 ppm
- Intermediate purity: the (C + N) interstitial content exceeds 150 ppm.

Although not usually mentioned in the alloy chemistry specifications, oxygen and hydrogen are also harmful, and these levels must be carefully restricted. Table 11.6 lists the compositions of some ultrahigh purity, intermediate purity, and standard-grade ferritic stainless steels.

The unique as-welded properties of the new ferritic stainless steels have been made possible by obtaining very low levels of impurities, including carbon, nitrogen, hydrogen, and oxygen, in the case of the alloys described as ultralow interstitials, and by obtaining a careful balance of niobium and/or titanium to match the carbon content in the case of alloys with intermediate levels of interstitials. For these reasons, every precaution must be taken, and welding procedures that optimize gas shielding and cleanliness must be selected to avoid pickup of carbon, nitrogen, hydrogen, and oxygen.

To achieve maximum corrosion resistance, as well as maximum toughness and ductility, the GTA welding process with a matching filler metal is usually specified; however, dissimilar high-alloy weld metals have also been successfully used. In this case, the choice of dissimilar filler metal must ensure the integrity of the ferritic metal system. Regardless of which of the new generation of ferritic stainless steels is to be welded, the following precautions are considered essential:

- First, the joint groove and adjacent surfaces must be thoroughly degreased with a solvent, such as acetone, that does not leave a residue. This will prevent pickup of impurities, especially carbon, before welding. The filler metal must also be handled carefully to prevent it from picking up

impurities. Solvent cleaning is also recommended. Under certain conditions, when using solvents, a fire hazard or health hazard may exist.

- Second, a welding torch with a large nozzle inside diameter, such as 19 mm (3/4 inch), and a gas lens (inert gas calming screen) is necessary. Pure, welding grade argon with a flow rate of 28 L/min (60 ft^3/h) is required for this size nozzle. In addition, the use of a trailing gas shield is beneficial, especially when welding heavy-gage materials. Use of these devices will drastically limit the pickup of nitrogen and oxygen during welding. Back gas shielding with argon is also essential. Procedures for welding austenitic stainless steels often recommend the use of nitrogen backing gas. Nitrogen must not be used when welding ferritic stainless steels. Standard GTA welding procedures used to weld stainless steels are inadequate and therefore must be avoided.
- Third, overheating and embrittlement by excessive grain growth in the weld and HAZ should be avoided by minimizing heat input. In multi-pass welds, overheating and embrittlement should be avoided by keeping the interpass temperature below 95 °C (200 °F).
- Lastly, to avoid embrittlement further, preheating (except to remove moisture) or postweld heat treating should not be performed. Postweld heat treatment is used only with the conventional ferritic stainless alloys.

11.3.1.17 Corrosion of Duplex Stainless Steel Weldments

In the wrought condition, duplex stainless steels have micro-structures consisting of a fairly even balance of austenite and ferrite. The new generation of duplex alloys are now being produced with low carbon and a nitrogen addition. These alloys are useful because of their good resistance to chloride SCC, pitting corrosion, and intergranular corrosion in the as-welded condition. Nominal compositions of some duplex stainless steels are given in Table 11.7.

The distribution of austenite and ferrite in the weld and HAZ is known to affect the corrosion properties and the mechanical properties of duplex stainless steels. To achieve this balance in properties, it is essential that both base metal and weld metal be of the proper composition. For example, without nickel enrichment in the filler rod, welds can be produced with ferrite levels in excess of 80%.

Such micro-structures have very poor ductility and inferior corrosion resistance. For this reason, autogenous welding (without the addition of filler metal) is not recommended unless postweld solution annealing is performed, which is not always practical. To achieve a balanced weld microstructure, a low carbon content and the addition of nitrogen (with Alloy 2205 at least 0.12% N) should be specified for the base metal.

Table 11.7 *Compositions of various duplex stainless steels*

UNS No.	Typicalalloy	Composition, % (Nominal unless otherwise indicated)									
		C	Cr	Cu	Fe	Mn	Mo	Ni	N	Si	Others
S31500	SAF 3RE60	0.03*	18.5	–	Balance	1.6	2.7	4.9	0.07	1.7	–
S32404	Uranus 50	0.04*	21.5	1.5	Balance	2*	2.5	7	0.1	1*	–
S31803	Alloy 2205	0.03*	22	–	Balance	2*	3	5.5	0.15	1*	–
S32304	SAF 2304	0.03*	23	–	Balance	2.5*		4	0.1	1*	–
S32900	Type 329 SS	0.2*	25.5	–	Balance	1*		3.75	–	0.75*	–
S31100	IN-744	0.05*	26	–	Balance	1*		6.5	–	0.6*	–
S31200	44LN	0.03*	25	–	Balance	2*		6.5	0.17	1*	–
S32950	7Mo-Plus	0.03*	27.5	–	Balance	2*		4.4	0.25	0.6*	–
S31260	DP-3	0. 3*	25	0.5	Balance	1*		6.5	0.2	0.75*	0.3 W
S32250	Ferralium Alloy 255	0.04*	25.5	1.7	Balance	1.5*		5.5	0.17	1*	–

*maxiumum

Low carbon helps to minimize the effects of sensitization, and the nitrogen slows the precipitation kinetics associated with the segregation of chromium and molybdenum during the welding operation. Nitrogen also enhances the reformation of austenite in the HAZ and weld metal during cooling.

These duplex alloys have been used in Europe for many years; therefore, guidelines relating to austenite-ferrite phase distribution are available. It has been shown that to ensure resistance to chloride SCC, welds should contain at least 25% ferrite. To maintain a good phase balance for corrosion resistance and mechanical properties (especially ductility and notch toughness) comparable to the base metal, the average ferrite content of the weld should not exceed 60%.

This means using welding techniques that minimize weld dilution, especially in the root pass. Conditions that encourage mixing of the lower-nickel base metal with the weld metal reduce the overall nickel content. Weld metal with a lower nickel content will have a higher ferrite content, with reduced mechanical and corrosion properties.

Once duplex base metal and welding consumables have been selected, it is then necessary to select joint designs and weld parameters that will produce welding heat inputs and cooling rates so as to produce a favorable balance of austenite and ferrite in the weld and HAZ.

Researchers have shown that the high-ferrite micro-structures that develop during welding in lean (low-nickel) base metal and weld metal compositions can be altered by adjusting welding heat input and cooling rate. In these cases, a higher heat input that produces a slower cooling rate can be used to advantage by allowing more time for ferrite to transform to austenite.

There are, however, some practical aspects to consider before applying higher heat inputs indiscriminately. For example, as heat input is increased, base metal dilution increases. As the amount of lower-nickel-based metal in the weld increases, the overall nickel content of the deposit decreases: this increases the potential for more ferrite, with a resultant loss in impact toughness, ductility, and corrosion resistance. This would be another case for using an enriched filler metal containing more nickel than the base metal.

Grain growth and the formation of embrittling phases are two other negative effects of high heat inputs. When there is uncertainty regarding the effect that welding conditions will have on corrosion performance and mechanical properties, a corrosion test is advisable.

The influence of different welding conditions on various material properties of Alloy 2205 has been studied.

11.3.1.18 Corrosion of Nickel and High-Nickel Alloy Weldments

The corrosion resistance of weldments is related to the micro-structural and micro-chemical changes resulting from thermal cycling. The effects of welding on the corrosion resistance of nickel-based alloys are similar to the effects on the corrosion resistance of austenitic stainless steels.

For example, sensitization due to carbide precipitation in the HAZ is a potential problem in both classes of alloys. However, in the case of nickel-based alloys, the high content of such alloying elements as chromium, molybdenum, tungsten, and niobium can result in the precipitation of other intermetallic phases, such as μ, σ, and η.

The characteristics of the various nickel-based alloys and the evolution of these alloys are discussed in later sections of this book. The corrosion resistance of weldments is dictated not only by the HAZ, but also by the weld metal itself. The effect of elemental segregation on weld metal corrosion must also be examined. The nickel-based alloys discussed later are the solid-solution alloys.

11.3.1.19 Corrosion of Aluminum Alloy Weldments

Variations in micro-structure across the weld and HAZ of aluminum weldments are known to produce susceptibility to corrosion in certain environments. These differences can be measured electrochemically and are an indication of the type of corrosion behavior that might be expected. Although some

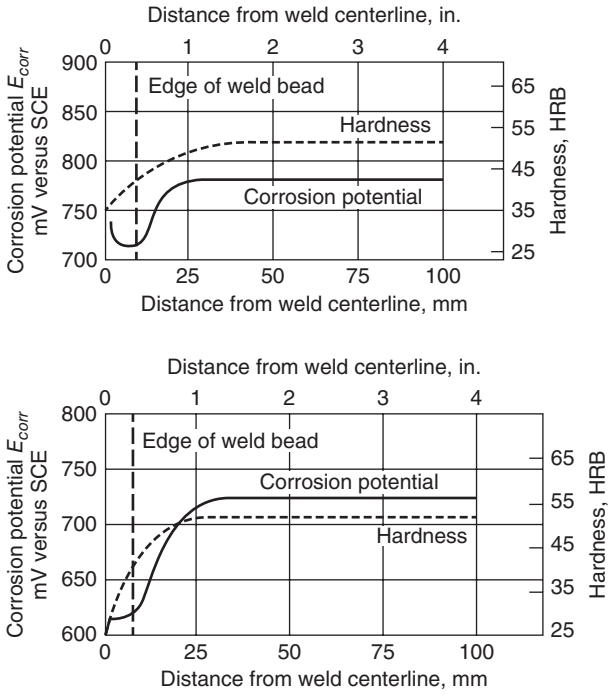


Figure 11.7 *Effect of the heat of welding on micro-structure, hardness, and corrosion potential of welded assemblies of two aluminum alloys. (Top) Alloy 5456-H321 base metal with Alloy 5556 filler, three-pass metal inert gas weld. (Bottom) Alloy 2219-T87 base metal with Alloy 2319 filler, two-pass tungsten inert gas weld. The differences in corrosion potential between the HAZ and the base metal can lead to selective corrosion. (Reproduced with permission from Daubert Cromwell.)*

aluminum alloys can be autogenously welded, the use of a filler metal is preferred to avoid cracking during welding and to optimize corrosion resistance.

The variations in corrosion potential (equilibrium potential) across three welds are shown in Figure 11.7 for Alloys 5456 and 2219. These differences can lead to localized corrosion. In general, the welding procedure that puts the least amount of heat into the metal has the least influence on micro-structure and the least chance of reducing the corrosion behavior of aluminum weldments.

Tables are available in *American Society for Metal*, (1984, p. 283) that summarize filler alloy selection recommended for welding various combinations of base metal alloys to obtain maximum properties, including corrosion resistance. Care must be taken not to extrapolate the corrosion performance ratings indiscriminately. Corrosion behavior ratings generally pertain only to the particular environment tested, usually rated in continuous or alternate immersion in fresh or salt water.

For example, the highest corrosion rating (A) is listed for use of Alloy 4043 filler to join Alloy 3003 to Alloy 6061. In strong (99%) nitric acid (HNO_3) service, however, a weldment made with Alloy 4043 filler would experience more rapid attack than a weldment made using Alloy 5556 filler. With certain alloys, particularly those of the heat-treatable 7000 series, thermal treatment after welding is sometimes used to obtain maximum corrosion resistance (Figure 11.8).

As with many other alloy systems, attention must be given to the threat of crevice corrosion under certain conditions. Strong (99%) HNO_3 is particularly aggressive toward weldments that are not made with full weld penetration.

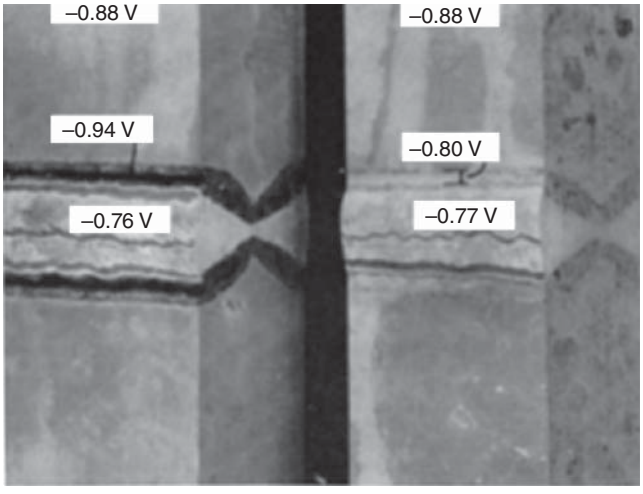


Figure 11.8 *Welded assemblies of aluminum Alloy 7005 with Alloy 5356 filler metal after a one-year exposure to seawater. (Reproduced with permission from Daubert Cromwell.)*

11.3.1.20 Corrosion of Tantalum and Tantalum Alloy Weldments

Examination of equipment fabricated from tantalum that has been used in a wide variety of service conditions and environments generally shows that the weld, HAZ, and base metal display equal resistance to corrosion. This same resistance has also been demonstrated in laboratory corrosion tests conducted in a number of different acids and other environments. However, in applications for tantalum-lined equipment, contamination of the tantalum with iron from underlying backing material, usually carbon steel, can severely impair the corrosion resistance of tantalum. About the only known reagents that rapidly attack tantalum are fluorine, HF and acidic solutions containing fluoride, fuming sulfuric acid (H_2SO_4) (oleum), which contains free sulfur trioxide (SO_3), and alkaline solutions.

An exception to the generalization that base metal and weldments in tantalum show the same corrosion resistance under aggressive media is discussed in the following example. Because tantalum is a reactive metal, the pickup of interstitial elements, such as oxygen, nitrogen, hydrogen and carbon, during welding can have a damaging effect on a refractory metal such as tantalum.

11.3.1.21 Preferential Pitting of a Tantalum Alloy Weldment in H_2SO_4 Service

A 76 mm (3 inch) diameter tantalum alloy tee removed from the bottom of an H_2SO_4 absorber that visually showed areas of severe etching attack was examined. The absorber had operated over a period of several months, during which time about 11 400 kg (25000 lb) of H_2SO_4 was handled. The absorber was operated at 60 °C (140 °F) with nominally 98% H_2SO_4. There was a possibility that some of the H_2SO_4 fed into the process stream may have been essentially anhydrous or even in the oleum range. Oleum is known to attack tantalum at temperatures only slightly higher than 60 °C (140 °F). In addition, the H_2SO_4 effluent was found to contain up to 5 ppm of fluoride.

11.3.1.22 Oxygen Tolerance of Tantalum Weldments

Tantalum reacts with oxygen, nitrogen, and hydrogen at elevated temperatures. The absorption of these interstitial elements, often called a gettering reaction, produces a sharp reduction in ductility

and can cause embrittlement. This impairment in ductility (and also in notch toughness, as manifested by an increase in ductile-to-brittle transition temperature) can be considered a form of corrosion. The other Group Va refractory metals (niobium and vanadium) and the Group IVa reactive metals (titanium, zirconium, and hafnium) can also suffer similar attack.

An investigation was conducted to determine the approximate tolerances of tantalum and Tantaloy "63" weldments for oxygen contamination that may be permitted during fabrication or subsequent service. Weldments of the materials were doped with various amounts of oxygen added either by anodizing or by oxidation in air. This was followed by vacuum annealing treatments to diffuse the oxygen through the sample cross section.

The oxygen concentration was monitored principally by hardness tests. Hardness is generally believed to be a better indicator of the extent of interstitial contamination than chemical analysis, which is subject to scatter and inaccuracy because of sampling difficulty. Bend tests (at room and liquid argon temperatures) and room-temperature Olsen cup formability tests were conducted to determine the hardness levels at which the materials embrittled.

The results showed that weldments of both materials remain ductile when hardened by interstitial contamination by oxygen up to Rockwell 30T hardness in the low 80s. Above this hardness, embrittlement may be expected.

The hardness level at which embrittlement occurs is substantially above the typical maximum allowable hardness of 65 HR30T specified for Tantaloy "63" or the 50 HR30T for tantalum flat mill products. Thus, if the extent of interstitial contamination by oxygen (and/or nitrogen) is controlled so that these maximum allowable hardness limits are not exceeded, embrittlement of weldments should not occur.

On the basis of chemical composition, the maximum oxygen tolerance for tantalum weldments appears to be about 400 to 550 ppm; for Tantaloy "63" weldments, it is about 350 to 500 ppm. Although commercially pure tantalum exhibits a somewhat higher tolerance for oxygen (and total interstitial contamination) than Tantaloy "63," the latter material appears to have somewhat better resistance to oxidation; this tends to offset the advantage tantalum has of a higher allowable oxygen pick-up before embrittlement occurs.

It should be further emphasized that the results are based on the assumption that oxygen was believed to be distributed relatively uniformly throughout the cross section in all parts of the weldment. A locally high concentration, such as a high surface contamination of oxygen or nitrogen, could result in a severe loss in ductility and could possibly even produce embrittlement.

Therefore, all handling, cleaning, and fabrication practices on tantalum and its alloys should avoid producing such surface contamination, as well as gross contamination. The section on corrosion of tantalum in this book gives more detailed information on the corrosion of tantalum and tantalum alloys.

11.4 Welding Procedure

All welding works should be according to the appropriate ASME Codes Section IX and/or relevant standards for fabrication of equipment, vessels, piping, etc.

11.4.1 Welding of Stainless Steels

The main problems encountered in welding stainless steels are the same as those seen in heat treatment. The heat of welding (portions of the base metal adjacent to the weld may be heated to 430 to 870 °C, (or 800 to 1600 °F) can cause sensitization and formation of intermetallic phases, thus

increasing the susceptibility of stainless steel weldments to intergranular corrosion, pitting, crevice corrosion, and SCC. These phenomena often occur in the heat-affected zone of the weld. Sensitization and intermetallic phase precipitation can be corrected by solution annealing after welding. Alternatively, low-carbon or stabilized grades may be used.

Another problem in high heat input welds is grain growth, particularly in ferritic stainless steels. Excessive grain growth can increase susceptibility to intergranular attack and reduce toughness. Thus, when welding most stainless steels, it is wise to limit weld heat input as much as possible.

11.4.2 Cleaning Procedures

Before any welding begins, all materials, chill bars, clamps, hold down bars, work tables, electrodes, and wire, as well as the stainless steel, must be cleaned of all foreign matter. Moisture can cause porosity in the weld that would reduce corrosion resistance. Organic materials, such as grease, paint, and oils, may result in carbide precipitation. Copper contamination may cause cracking. Other shop dirt can cause weld porosity and poor welds in general.

11.4.3 Weld Design and Procedure

Weld design and procedure are very important in producing a sound corrosion-resistant weld. Good fit and minimal out-of-position welding will minimize crevices and slag entrapment. The design should not place welds in critical flow areas. When attaching such devices as low-alloy steel supports and ladders on the outside of a stainless steel tank, a stainless steel intermediate pad should be used. In general, stainless steels with higher alloy content than Type 316 should be welded with weld metal richer in chromium, nickel, and molybdenum than the base metal. Every attempt should be made to minimize weld spatter.

After welding, all weld spatter, slag, and oxides should be removed by brushing, blasting, grinding, or chipping. All finishing equipment must be free of iron contamination. It is advisable to follow the mechanical cleaning and finishing with a chemical cleaning. Such a cleaning will remove any foreign particles that may have been embedded in the surface during mechanical cleaning without attacking the weldment. More information on welding of stainless steels is available in Volume 6 of the 9th Edition of *Metals Handbook*, ASM.

11.4.4 Weld Defects

There is no guarantee that crack-free joints will automatically be obtained when fabricating "weldable" metals. This is a result of the fact that weldability is not a specific material property, but a combination of the properties of the parent metals, filler metal (if used), and various other factors (see Table 11.8).

The consequence of the average structural material possessing imperfect weldability is to produce a situation where defects may arise in the weld deposit or heat-affected zone (see Figure 11.9 and Table 11.9). Table 11.10 shows some Possible problems in less commonly welded metals.

11.4.5 Carbon and Low-Alloy Steels

These usually present little problem since the parent and filler metals are generally of similar composition, although there is some evidence that the precise electrode type in manual metal arc welding for marine conditions may be important; weld metal deposited from basic-coated rods appears to corrode more rapidly than that deposited from rutile-based coatings.

Table 11.8 *Factors affecting weldability*

Parent metal	Filler metal	Other factors
Composition	Composition	Degree of fusion
Thickness	Impact strength	Joint formation
State of heat treatment	Toughness	Degree of restraint
Toughness	Hydrogen content	Form factor (Transition)
Temperature	Purity	Deposition technique
Purity	Homogeneity	Skill and reliability of the welder
Homogeneity	Electrode diameter (Heat input during welding)	

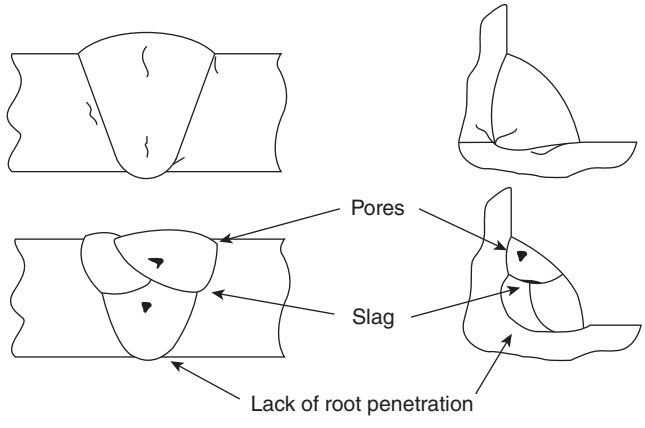


Figure 11.9 *Typical weld defects.*

Table 11.9 *Weldability defects*

Defect	Causes	Remedies
Hot cracks	Large solidifiation range	More crack-proof filler
	Segregation	Less fusion
	Stress	
Underbead cracks	Hardenable parent plate	Low hydrogen process
	Hydrogen	Planned bead sequence
	Stress	Preheating
Microfissures	Hardenable deposit	Low hydrogen process
	Hydrogen	Pre-and post-heating
	Stress	
Toe cracks	High stress	Planned bead sequence
	Notches	Preheating
	Hardenable parent plate	Avoidance of notches
Hot tears	Segregation	Less fusion
	Stress	Cleaner parent plate
Porosity	Gas absorption	Remove surface scale
		Remove surface moisture
		Cleaner gas shield

Table 11.10 *Possible problems in less commonly welded metals*

Metal	Weldability	Corrosion
Copper alloys	Porosity	De-zincification
	Hot cracking	De-aluminification
	Hot tearing	Stress corrosion
	Steam explosion	
Magnesium alloys	Porosity	Stress corrosion
	Hot cracking	Pitting
	Lack of fusion	
Titanium alloys	Porosity	Stress corrosion
	Embrittlement	

An environment containing H_2S, cyanides, nitrates, or alkalis may produce stress-corrosion cracking in highly stressed structures and these should be first stress-relieved by heating to 650 °C.

An interesting development in weldable corrosion-resistant steels is the copper-bearing or weathering steels, which exhibit enhanced corrosion resistance in industrial atmospheres in the unpainted condition. For optimum corrosion resistance after welding, the filler employed should be suitably alloyed to give a deposit of composition similar to that of the steel plate.

11.4.6 Stainless steels

Since stainless steels are widely used for resisting corrosive environments, it is relevant to consider the welding of these alloys in some detail. There are three groups of stainless steels, each possessing their own characteristic welding problem:

- *Ferritic type*: welding produces a brittle deposit and a brittle heat-affected zone caused by the very large grain size that is produced. The problem may be reduced in severity by the use of austenitic filler and/or the application of pre- and postweld heat treatments: the latter is a serious limitation when large welded structures are involved.
- *Martensitic type*: heat-affected zone cracking is likely and may be remedied by employing the normal measures required for the control of hydrogen-induced cracking.
- *Austenitic type*: these are susceptible to hot cracking, which may be overcome by balancing the weld metal composition to allow the formation of a small amount of δ -Fe (ferrite) in the deposit, optimum crack resistance being achieved with a δ -Fe content of 5–10%. More than this concentration increases the possibility of δ-phase formation if the weldment is used at elevated temperature with a concomitant reduction in both mechanical and corrosion resistance.

The main problems that might be encountered in stainless steel are weld decay, knifeline attack and stress-corrosion cracking (Figure 11.10).

Weld decay is the result of the intergranular precipitation of chromium carbide in the temperature range 430–870 °C and material in this condition is referred to as being "sensitized." Sensitization depletes the matrix in the grain-boundary region of chromium and this region may eventually suffer intergranular corrosion. In corrosive environments some zone in the vicinity of the weld area is inevitably raised to within the sensitization temperature range and the degree of severity of sensitization will be dependent on a number of process factors that determine the time in this temperature range, e.g. heat input, thickness of plate. For most commercial grades of stainless steel in thin section (< 10 mm) the loss in corrosion resistance is slight and seldom warrants any special measures. For a

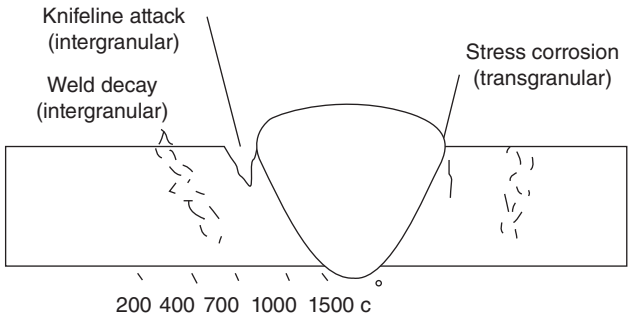


Figure 11.10 *Corrosion sites in stainless steel welds. The typical peak temperatures attained during welding (°C) are given at the foot of the diagram.(Note that knifeline attack has the appearance of a sharply defined line adjacent to the fusion zone.)*

high degree of corrosion resistance, or in welded thick plate, it becomes necessary to take one of the following courses of action:

- Thermally treat the structures to effect a resolution of the chromium carbide; this is often impractical in large structures unless local heat treatment is employed, but is not always satisfactory since a sensitized zone could be produced just outside the local thermally treated region
- Use extra-low-carbon steel
- Use stabilized steels, i.e. austenitic steels containing niobium, tantalum, or titanium.

11.4.7 Nickel Alloys

In the main, welding does not seriously affect the corrosion resistance of the high-nickel alloys and stress relief is not generally required since the resistance to stress corrosion is particularly high; this property increases with increase in nickel content and further improvement may be obtained by the addition of silicon. The chromium-containing alloys can be susceptible to weld decay and should be thermally stabilized with titanium or niobium, and where conditions demand exposure to corrosive media at high temperatures, a further postweld heat treatment may be desirable. For the Ni-Cr-Mo-Fe-W-type alloys, it is suggested that the material should be given a two-stage heat treatment prior to single-pass welding in order to produce a dependable micro-structure with a thermally stabilized precipitate.

The Ni-28Mo alloy provides a special case of selective corrosion analogous to the weld-decay type of attack; it may be removed by solution treatment or using an alloy containing 2% vanadium.

Of the weldability problems, nickel and nickel-based alloys are particularly prone to solidification porosity, especially if nitrogen is present in the arc atmosphere, but this may be controlled by ensuring the presence of titanium as a denitrider in the filler and maintaining a short arc length. The other problem that may be encountered is hot cracking, particularly in alloys containing Cr, Si, Ti, Al, B, Zr, S, Pb, and P.

For optimum corrosion resistance it is recommended that similar composition fillers be used wherever possible, and obviously any flux residues that may be present must be removed.

11.4.8 Aluminum Alloys

These alloys are very susceptible to hot cracking and in order to overcome this problem most alloys have to be welded with a compensating filler of different composition from that of the parent alloy,

Table 11.11 *Typical joining processes*

Joining process	Types
Mechanical fasteners	Nuts, bolts, rivets, and screws
Soldering and brazing	Hot iron, torch, furnace, and vacuum
Fusion welding	Oxyacetylene, manual metal arc, tungsten inert gas, metal inert gas, carbon dioxide, pulsed arc, fused arc, submerged arc, electro slag, and electron beam
Resistance welding	Spot, seam, stitch, projection, butt, and flash butt
Solid-phase welding	Pressure, friction, ultrasonic, and explosive

and this difference in composition may lead to galvanic corrosion. A further problem in the welding of these materials is the high solubility of the molten weld metal for gaseous hydrogen, which causes extensive porosity in the seam on solidification; the only effective remedy is to maintain the hydrogen potential of the arc atmosphere at a minimum by using a hydrogen-free gas shield with dry, clean consumables (e.g. welding rods, wire) and parent plate.

In general, the corrosion resistance of many of the alloys is not reduced by welding. Any adverse effects that may be encountered with the high-strength alloys can be largely corrected by post-weld heat treatment; this is particularly true of the copper-bearing alloys. Pure aluminum fillers impart the best corrosion resistance, although the stronger Al-Mg and Al-Mg-Si fillers are normally suitable; the copper-bearing fillers are not particularly suitable for use in a corrosive environment. Resistance welding does not usually affect the corrosion resistance of the aluminum alloys.

The heat-affected zone may become susceptible to stress-corrosion cracking, particularly the high-strength alloys, and expert advice is necessary concerning the suitability of a particular alloy for a certain environment after welding. In this context Al-Zn-Mg-type alloys have been extensively studied and it has been shown that maximum sensitivity appears to occur when there is a well-developed precipitation at the heat-affected zone grain boundaries adjacent to the fusion line, a fine precipitate within the grain and a precipitate-free zone immediately adjacent the grain boundaries. The action of stress-corrosion cracking then appears to be a result of local deformation in the precipitate-free zone combined with the anodic character of the precipitate particles.

11.4.9 Other Materials for Welding

Suggestions are made in Table 11.11. It is sufficient to state that with a knowledge of the general characteristics of welding process and its effects on a metal a reliable joint for a particular problem will normally be the rule and not the exception.

11.5 Welding and Joining

A jointed fabrication is one in which two or more components are held in position:

- by means of a mechanical fastener (screw, rivet, or bolt)
- by welding, brazing, or soldering
- by an adhesive.

The components of the joint may be metals of similar or dissimilar composition and structure, metals and non-metals or they may be wholly non-metallic. Since the majority of fabrications are joined

at some stage of their manufacture, the corrosion behavior of joints is of the utmost importance, and the nature of the metals involved in the joint and the geometry of the joint may lead to situations in which one of the metals is subjected to accelerated and localized attack. Although corrosion at bimetallic contacts involving different metals has been dealt with in the relevant standards, it is necessary to emphasize the following in relation to corrosion at joints in which the metals involved may be either identical or similar:

- A difference in potential may result from differences in structure or stress brought about during or subsequent to the joining process.
- Large differences in area may exist in certain jointed structures, e.g. when fastening is used.
- Furthermore, many joining processes lead to a crevice, with the consequent possibility of crevice corrosion.
- Before considering the factors that lead to corrosion it is necessary to examine briefly the basic operations of joint manufacture.
- For joining dissimilar metals insulating washers, insulating gaskets, and insulating sleeves should be used, as required.

11.5.1 Mechanical Fasteners

These require little description and take the form of bolts, screws, rivets, etc. Mechanical failure may occur as a result of the applied stress in shear or tension exceeding the ultimate strength of the fastener, and can normally be ascribed to poor design, although the possibility of the failure of steel fittings at ambient or sub-zero temperatures by brittle fracture, or at ambient temperatures by hydrogen embrittlement, cannot be ignored. If brittle failure is a problem then it can be overcome by changing the joint design or employing a fastener having a composition with better duetility transition properties.

11.5.2 Joining, Brazing, and Soldering

11.5.2.1 Joining

Joining differs from all other construction methods in that an attempt is made to produce a continuity of homogeneous material that may or may not involve the incorporation of filler material. There are a large variety of processes by which this may be achieved, most of which depend upon the application of thermal energy to bring about a plastic or molten state of the metal surfaces to be joined. The more common processes of welding compared with mechanical fasteners, soldering, and brazing are classified in Table 11.11.

The macrographic examination of a welded joint shows two distinct zones, namely the fusion zone with its immediate surroundings and the parent metal. It is apparent therefore, that such processes produce differences in micro-structure between the cast deposit, the heat-affected zone, which has undergone a variety of thermal cycles, and the parent plate. Figure 11.11 shows the basics of weld definition.

11.5.3 Protection of welded joints

Structural steels are frequently protected from corrosion by means of a paint primer, but these materials can have an adverse effect on the subsequent welding behavior and this is mainly observed as porosity. Hot-dip galvanising for longterm protection can also lead to porosity and intergranular cracking after welding, in which case it may be necessary to remove the zinc coating from the faying edges prior to welding. The presence of zinc can also lead to operator problems due to the toxicity of the fume evolved unless adequate fume extraction is employed.

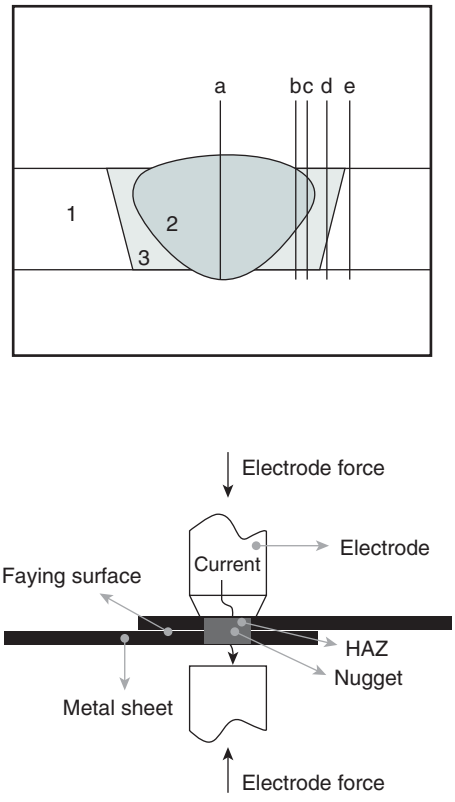


Figure 11.11 *Weld definitions. (Top) Fusion welding: a – center of weld metal; b – fusion line; c – fusion line +1 mm; d – fusion line +3 mm; e – fusion line +5 mm; 1 – parent metal; 2 – weld; 3 – HAZ. (Bottom) Resistance spot welding.*

Prior to painting, all welding residues must be removed and the surface prepared by grinding, grit blasting, wire brushing or chemical treatment. This preparation is of fundamental importance, the method of applying the paint and the smoothness of the bead apparently having little effect on the final result.

11.5.4 Pressure Pipe Brazing and Soldering

11.5.4.1 Brazing Qualification

The qualification of brazing procedures, brazers, and brazing operators should be in accordance with the requirements of the Boilers and Pressure Vessels (BPV) Code, ASME Section IX, Part QB. For Category D Fluid service at design temperature not over 93 °C (200 °F), such qualification is at the owner's descretion.

11.5.4.2 Brazing and Soldering Materials

- *Filler metal*: The brazing alloy or solder should melt and flow freely within the specified or desired temperature range and, in conjunction with a suitable flux or controlled atmosphere, should wet and adhere to the surfaces to be joined.

- *Flux*: A flux that is fluid and chemically active at brazing or soldering temperature should be used when necessary to eliminate oxidation of the filler metal and the surfaces to be joined, and to promote free flow of brazing alloy or solder.

11.5.4.3 Preparation

- *Surface preparation*: The surfaces to be brazed or soldered should be clean and free from grease, oxides, paint, scale, and dirt of any kind. A suitable chemical or mechanical cleaning method should be used if necessary to provide a clean wettable surface.
- *Joint clearance*: The clearance between surfaces to be joined by soldering or brazing should be no larger than necessary to allow complete capillary distribution of the filler metal.

11.5.4.4 Requirements

- *Soldering procedure*: Solderers should follow the procedure in the *Copper Tube Handbook* of the Copper Development Association or other approved procedures.
- *Heating*: To minimize oxidation, the joint should be brought to brazing or soldering temperature in as short a time as possible without localized underheating or overheating.
- *Flux removal*: Residual flux should be removed if detrimental.

11.6 Soldered Joints

Soldering and brazing are methods of joining components together with a lower-melting-point alloy so that the parent metal (the metal or metals to be joined) is not melted (Table 11.12). In the case of soft soldering, the maximum temperature employed is usually of the order of 250 °C and the filler

Table 11.12 *Soldering and brazing*

Process	Temperature range, °C	Typical filters	Fluxes
Soldering			
Hot iron	60–300 °C	70pb-30sn	Chloride-based
Oven		40pb-60sn	Fluoride-based
Ultrasonic		70pb-27sn-3sb	Resin-based
Dip		40pb-58sn-2sb	
Resistance		sn-zn-pb	
Wave and cascade			
Brazing			
Torch	500–1200 °C	90AL-10SI	Borax-based
Dip		50Ag-15Cu-17Zn-18Cd	Fluoride-based
Salt bath		Ag-Cu-Na-In	Hydrogen gas
Furnace		60Ag-30Cu-10Zn	Town gas
Induction		50Cu-50Zn	Vacuum
Resistance		97Cu-3F	
		70Ni-17Cr-3B-10Fe	
		82Ni-7Cr-5Si-3Fe	
		60Pd-40Ni	

alloys (used for joining) are generally based on the tin–lead system. The components must present a clean surface to the solder to allow efficient wetting and flow of the molten filler and to provide a joint of adequate mechanical strength.

To obtain the necessary cleanliness, degreasing and mechanical abrasion may be required followed by the use of a flux to remove any remaining oxide film and to ensure that no tarnish film develops on subsequent heating.

In the case of carbon steels and stainless steels, and many of the non-ferrous alloys, the fluxes are based on acidic inorganic salts, e.g. chlorides, which are highly corrosive to the metal, unless they are removed subsequently by washing in hot water. For soldering tinplate, clean copper, and brass, it is possible to formulate rosin-based fluxes having non-corrosive residues, and these are essential for all electrical and electronic work.

Activators are added to the rosin to increase the reaction rate, but these must be such that they are thermally decomposed at the soldering temperature if subsequent corrosion is to be avoided. Corrosion is always a risk with soldered joints in aluminum, owing to the difference in electrical potential between the filler alloy and the parent metal, and the highly corrosive nature of the flux that is generally used for soldering. However, it is possible to employ ultrasonic soldering to eliminate use of flux. With aluminum soldering it is imperative that the joints be well cleaned both before and after the soldering operation, and the design should avoid subsequent trapping of moisture.

11.7 Brazed Joints

When stronger joints are required, brazing may be used. The filler alloys employed generally melt at much higher temperatures (600–1200 °C), but the effectiveness of the joining process still depends upon the surface cleanliness of the components to ensure adequate wetting and spreading.

Metallurgical and mechanical hazards may be encountered in that the filler may show poor spreading or joint-filling capacity in a certain situation or may suffer from hot tearing, whilst during furnace brazing in hydrogen-containing atmospheres there is always the possibility that the parent metal may be susceptible to hydrogen embrittlement or steam cracking.

Furthermore, brittle diffusion products may be produced at the filler–base-metal interface as a result of the reaction of a component of the filler alloy with a base-metal component, e.g. phosphorus-bearing fillers used for steel in which the phosphorus diffuses into the steel.

Serious damage can be caused by:

- diffusion into the parent metal of the molten brazing alloy itself when either one or both of the parent metal(s) is in a stressed condition induced by previous heat treatment or cold working,
- an externally applied load, which need only be the weight of the workpiece.

Nickel and nickel-rich alloys are particularly prone to liquid-braze-filler attack especially when using silver-based braze fillers at temperatures well below the annealing temperature of the base metal, since under these conditions there is then no adequate stress relief of the parent metal at the brazing temperature. The problem may be avoided by annealing prior to brazing and ensuring the maintenance of stress-free conditions throughout the brazing cycle.

There is a whole range of silver–nickel and palladium-based braze fillers of high oxidation and corrosion resistance that have been developed for joining the nickel-rich alloys; however, the presence of sulfur, lead, or phosphorus in the base-metal surface or in the filler can be harmful, since quite small amounts can lead to interface embrittlement.

In the case of the Monels, the corrosion resistance of the joint is generally less than that of the parent metal and the design must be such that as little as possible of the joint is exposed to the corrosive media.

When, in an engineering structure, the aluminum–bronzes are used for their corrosion resistance, the selection of braze filler becomes important and although the copper–zinc brazing alloys are widely used, the corrosion resistance of the joint will be that of the equivalent brass rather than that of the bronze.

With the carbon and low-alloy steels, the braze fillers are invariably noble to the steel so that there is little likelihood of trouble (small cathode/large anode system), but for stainless steels a high-silver braze filler alloy is desirable for retaining the corrosion resistance of the joint, although stress-corrosion cracking of the filler is always a possibility if the latter contains any zinc, cadmium, or tin.

An interesting example of judicious choice of braze filler is to be found in the selection of silver alloys for the brazing of stainless steels to be subsequently used in a tap-water environment. Although the brazed joint may appear to be quite satisfactory, after a relatively short exposure period, failure of the joint occurs by a mechanism that appears to be due to the breakdown of the bond between the filler and the braze metal. De-zincification is a prominent feature of the phenomenon and zinc-free braze alloys based on the Ag-Cu system, with the addition of nickel and tin, have been found to inhibit this form of attack. A similar result is obtained by electroplating 0.007 mm of nickel over the joint area prior to brazing with a more conventional Ag-Cu-Zn-Cd alloy.

Brazing is generally considered unsuitable for equipment exposed to ammonia and various ammoniacal solutions because of the aggressiveness of ammonia to copper- and nickel-based alloys, but recently an alloy based on Fe-3.25B-4.40Si-50.25Ni has been shown to be suitable for such applications.

Study of the marine corrosion behavior of a number of braze-alloy–parent-metal combinations has shown that compatibility is a function of the compositions of the filler and parent metals, their micro-structures and chance factors such as overheating during the brazing operation.

11.8 Pipe Bending and Forming

Pipe may be bent and components may be formed by any hot or cold method that is suitable for the material, the fluid service, and the severity of the bending or forming process. The finished surface should be free of cracks and substantially free from buckling. Thickness after bending or forming should be not less than that required by the design.

11.8.1 Bending

- *Bend flattening*: Flattening of a bend, the difference between maximum and minimum diameters at any cross section, should not exceed 8% of nominal outside diameter for internal pressure and 3% for external pressure.
- *Bending temperature*: Cold bending of ferritic materials should be done at a temperature below the transformation range. Hot bending should be done at a temperature above the transformation range and in any case within a temperature range consistent with the material and the intended service.
- *Corrugated and other bends*: Dimensions and configuration should conform to the design.

Table 11.13 *Requirements for heat treatment after welding*

P-Number*	Holding temperature range, °F (°C)	Holding time based on nominal thickness	
		Up to 2 inches (50 mm)	Over 2 inches (50 mm)
P-No-1 Gr-Nos. 1,2,3	1100 (600)–1200 (650)	1h/inch (25 mm) 15 minutesmin.	2 h plus 15 minfor each additionalinch over 2 inches (50 mm)
Postwelding heat treatment (PWHT) of P-No-1 materials is not mandatory, provided that all of the following conditions are met: • The nominal thickness, is 3/4 inch (19.0 mm) or less • A minimum preheat of 200 °F (95 °C) is applied when the nominal material thickness of either of the base metals exceeds 1 inch (25 mm).			
P-No-3 Gr-Nos. 1,2	1100 (600)–200 (650)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
PWHT of P-No-3 materials is not mandatory, provided that all of the following conditions are met: • The nominal thickness, as defined, is 5/8 inches (16.0 mm) or less • A minimum preheat of 200 °F (95 °C) is applied when the nominal material thickness of either of the base metals exceeds 5/8 inches (16 mm) • The specified carbon content of the PNo-3 base material is 0.25% or less.			
P-No-4 Gr-Nos. 1,2	1200 (650)–1300 (700)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
PWHT is not mandatory for PNo-4 material under the following conditions: • Welds in pipe or attachment welds to pipe complying with all of the following conditions: • A nominal material thickness of 1/2 inch (13 mm) or less. • A specified carbon content of the material to be welded of 0.15% or less. • Application of 250 °F (120 °C) minimum preheat during welding. • For seal welding of threaded or other mechanical joints provided. • The seal weld has a throat thickness of 3/8 inch (9 mm) or less. • A minimum preheat of 250 °F (120 °C) is maintained during welding. • The thickness of the test plate used in making the welding procedure qualification of section IX should not be less than that of the material to be welded. • The attachment weld has a throat thickness of 3/16 inches or less.			
P-No-5A Gr-Nos. 1	1300 (700)–1400 (760)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
PWHT is not mandatory for P-No-5A material under the following conditions: • Welds in pipe or attachment welds to pipe complying with all of the following conditions: • A nominal material thickness of 1/2 inch (13 mm) or less • A specified carbon content of the material to be welded of 0.15% or less • A minimum preheat of 300 °F (150 °C) is maintained during welding. • Attachment welds for non-load carrying attachments provided in addition to the above: • The hardened portion of the heat affected zone (HAZ) should not encroach on the minimum wall thickness of pipe, as determined by welding procedure qualification using the maximum welding heat input. The depth of the HAZ should be taken as the point where the HAZ hardness does not exceed the average unaffected base-metal hardness by more than 10%. • The thickness of the test plate used in making the welding procedure qualification should not be less than that of the material to be welded. • The attachment weld has a throat thickness of 3/16 inch or less.			

(*continued overleaf*)

Table 11.13 *(continued)*

P-Number*	Holding temperature range, °F (°C)	Holding time based on nominal thickness	
		Up to 2 inches (50 mm)	Over 2 inches (50 mm)
P-No-5B Gr-Nos. 1,2	1300 (700)–1400 (760)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
P-No-6 Gr-Nos. 1,2,3	1400 (760)–1475 (800)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
PWHT is not mandatory for P-No-6 type 410 material provided all of the following conditions are met: • The specified carbon content is not more than 0.08% • The nominal material thickness is 3/8 inches (10 mm) or less • The weld is made with A8, A9, F43 filler metal.			
P-No-7 Gr-Nos. 1,2	1350 (730)–1425 (775)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
In lieu of the cooling rate described, P-No-7 material cooling rate should be not greater than 100 °F (55 °C) per h in the range above 1200 °F (650 °C), after which the cooling rate should be sufficiently rapid to prevent embitterment. PWHT is not mandatory for P-No-7 type 405 material provided all of the following conditions are met: • The specified carbon content is not more than 0.08% • The nominal material thickness is 3/8 inch (10 mm) or less.			
P-No-9A Gr-No. 1	1100 (600)–1200 (650)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
PWHT is not mandatory for P-No-9A material when welds on pipe or attachment welds to pipe comply with all of the following conditions: • A nominal material thickness of 1/2 inch (13 mm) or less. • A specified carbon content of the material to be welded of 0.15% or less • A minimum preheat of 250 °F (120 °C) is maintained during welding. When it is impractical to PWHT at the temperature range specified, it is permissible to perform the PWHT of this material at lower temperature for longer periods of time but the minimum PWHT should not be less than 1000 °F (550 °C)			
P-No-9B Gr-No. 1	1100 (600)–1175 (630)	1h/inch (25 mm) 15 minutes min.	2 h plus 15 min for each additional inch over 2 inches (50 mm)
PHWT of P-No-9B material is not mandatory for a nominal material thickness of 5/8 inch (16 mm) or less, provided the welding procedure qualification has been made using material of thickness equal to or greater than the production weld. When it is impractical to PWHT at the temperature range specified, it is permissible to perform the PWHT of this material at lower temperatures for longer periods of time, but the minimum PWHT temperature should not be less than 1000 °F (550 °C)			

Table 11.13 *(continued)*

P-Number*	Holding temperature range, °F (°C)	Holding time based on nominal thickness	
		Up to 2 inches (50 mm)	Over 2 inches (50 mm)
P-No-101 Gr-No. 1	1350 (730)–1500 (815)	1h/inch (25 mm) 15 minutes min.	1 h/inch (25 mm)
In lieu of the cooling rate, the P-No-101 material cooling rate should be not greater than 100 °F/h in the range above 1200 °F (650 °C), after which the cooling rate should be sufficiently rapid to prevent embrittlement. Postweld heat treatment is neither required nor prohibited for a nominal thickness of $^1/_2$ inch or less.			

*P-Number from ASME, BPV Code, (Boilers and pressure vessels code) Section IX, Table QW-422. Special P-Numbers (SP- 1, SP-2, SP-3, SP-4, and SP-5) require special consideration. The required thermal treatment for Special P-Numbers should be established by the engineering design and demonstrated by the welding procedure qualification

11.8.2 Forming

The temperature range for forming should be consistent with material, intended service, and specified heat treatment.

Heat treatment should be performed when required by the following:

- Hot bending and forming: After hot bending and forming, heat treatment is required for P-Nos. 4, 5, 6, and 10A materials in all thicknesses.
- Cold bending and forming: After cold bending and forming, heat treatment is required (for all thicknesses, and with temperature and duration as given in Table 11.13 when any of the following conditions exist:
  - For P-Nos. 1–6 materials in Table 11.13, where the maximum calculated fiber elongation after bending or forming exceeds 50% of the specified basic minimum elongation (in the direction of severest forming) for the applicable specification, grade, and thickness. This requirement may be waived if it can be demonstrated that the selection of pipe and the choice of bending or forming process provides assurance that, in the finished condition, the most severely strained material retains at least 10% elongation.
  - For any material requiring impact testing, where the maximum calculated fiber elongation after bending or forming will exceed 5%.
  - When specified in the engineering design.

12
Heat Treatment

Many of the mechanical properties of materials are improved by various heat treatments. Unfortunately, such properties as hardness and strength are often achieved at the expense of corrosion resistance. For example, the hardness and strength of martensitic steels are counterbalanced by a lower corrosion resistance than for the ferritic and austenitic steels. The very high strengths achieved for precipitation-hardened steels are due to the secondary precipitates formed during the solution heat treating and aging process. Precipitates with electrochemical properties distinctly different from those of the matrix have a deleterious effect on corrosion.

Processes such as cold working, in which the material is plastically deformed into some desired shape, lead to the formation of elongated and highly deformed grains and a decrease in corrosion resistance. Cold working can also introduce residual stresses that make the material susceptible to stress-corrosion cracking. An improvement in corrosion resistance can be achieved by subsequently annealing at a temperature at which grain recrystallization can occur. A partial anneal leads to stress relief without a major effect on the overall strength of the material.

From the corrosion viewpoint, welding is a particularly troublesome treatment. Because welding involves the local heating of a material, it can lead to phase transformations and the formation of secondary precipitates. It can also induce stress in and around the weld. Such changes can lead to significant local differences in electro-chemical properties, as well as the onset of such processes as intergranular corrosion. Therefore, the weld filler metal should be as close in electro-chemical properties to the base metal as technically feasible, and the weld should be subsequently stress relieved.

Heat treatment should be used to avert or relieve the detrimental effects of high temperature and severe temperature gradients inherent in welding, and to relieve residual stresses created by bending and forming.

12.1 General Heat Treatment Requirements

Heat treatment to be used after production welding should be specified in the Welding Procedure Specification (WPS) and should be used in qualifying the welding procedure. The engineering design

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should specify the examination and/or other production quality control to ensure that the final welds are of adequate quality.

12.1.1 Governing Thickness

When components are joined by welding, the thickness to be used in applying the heat treatment provisions should be that of the thicker component measured at the joint, except as follows.

In the case of branch connections, metal (other than weld metal) added as reinforcement, whether an integral part of a branch fitting or attached as a reinforcing pad or saddle, should not be considered in determining heat treatment requirements. Heat treatment is required, however, when the thickness through the weld in any plane through the branch is greater than twice the minimum material thickness requiring heat treatment, even though the thickness of the components at the joint is less than the minimum thickness. Thickness through the weld for the details shown in Figure 12.1 should be computed using the following formulas:

$$\text{Sketch (1)} = T_b + t_c$$

$$\text{Sketch (2)} = T_h + t_c$$

$$\text{Sketch (3)} = \text{greater of } T_b + t_c \text{ or } T_h + t_c$$

$$\text{Sketch (4)} = Th + T_r + t_c$$

$$\text{Sketch (5)} = T_b + t_c$$

where:
T_b = nominal thickness of branch pipe
T_h = nominal thickness of header
t_c = check (ok) of 0.7 T_b
T_r = nominal thickness of reinforcing pad or saddle.

In the case of fillet welds at slip-on and socket welding flanges and piping connections NPS 2 and smaller, for seal welding of threaded joints in piping NPS 2 and smaller, and for attachment of external non-pressure parts such as lugs or other pipe supporting elements in all pipe sizes, heat treatment is required when the thickness through the weld in any plane is more than twice the minimum material thickness requiring heat treatment (even though the thickness of the components at the joint is less than that minimum thickness) except as follows:

- Not required for P-No. 1 materials when weld throat thickness is 16 mm (5/8 inch) or less, regardless of base metal thickness
- Not required for P-No. 3, 4, 5, or 10A materials (see Table 11.13) when weld throat thickness is 13 mm (1/2 inch) or less, regardless of base metal thickness, provided that not less than the recommended preheat is applied, and the specified minimum tensile strength of the base metal is less than 490 MPa (71 ksi)
- Not required for ferritic materials when welds are made with filler metal which does not air harden. Austenitic welding materials may be used for welds to ferritic materials when the effects of service conditions, such as differential thermal expansion due to elevated temperature, or corrosion, will not adversely affect the weldment.

12.1.2 Heating and Cooling

The heating method should provide the required metal temperature, metal temperature uniformity, and temperature control, and may include an enclosed furnace, local flame heating, electric resistance,

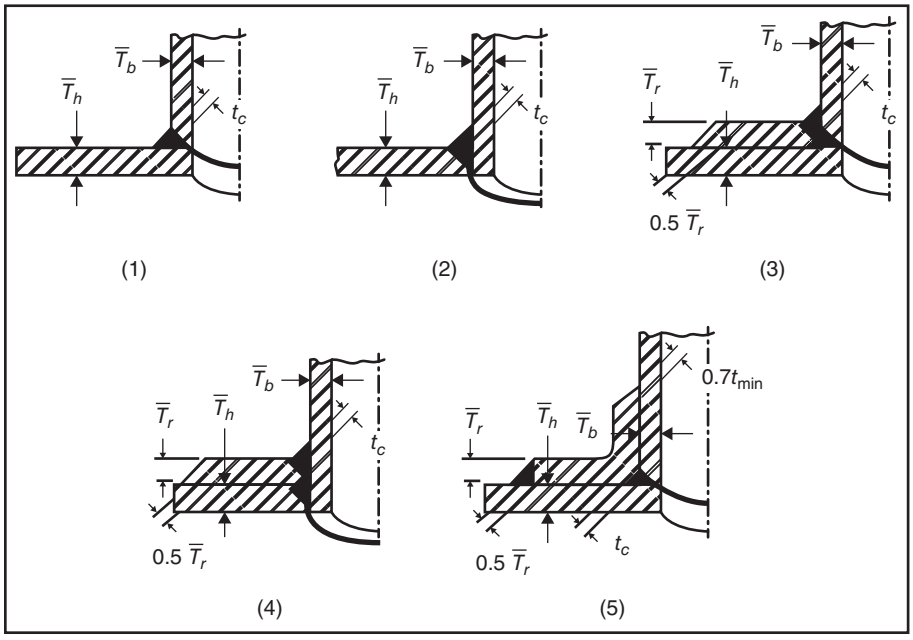


Figure 12.1 *Acceptable details for branch attachment welds.*

electric induction, or exothermic chemical reaction. The cooling method should provide the required or desired cooling rate and may include cooling in a furnace, in air, by application of local heat or insulation, or by other suitable means.

12.1.3 Temperature Verification

Heat treatment temperature should be checked by thermocouple pyrometers or other suitable methods to ensure that the Welding Procedure Specification (WPS) requirements are met.

12.1.4 Hardness Tests

Hardness tests of production welds and of hot-bent and hot-formed piping are intended to verify satisfactory heat treatment. The hardness limit applies to the weld and to the heat-affected zone (HAZ) tested as close as practicable to the edge of the weld:

- Where a hardness limit is specified in Table 11.13 at least 10% of welds, hot bends, and hot-formed components in each furnace heat treated batch and 100% of those locally heat treated should be tested.
- When dissimilar metals are joined by welding, the hardness limits specified for the base and welding materials in Table 11.13 should be met for each material.

12.1.5 Specific Requirements of Heat Treatment

Where warranted by experience or knowledge of service conditions, alternative methods of heat treatment or exceptions to the basic heat treatment provisions may be adopted.

12.1.6 Alternative Heat Treatment

Normalizing, or normalizing and tempering, or annealing may be applied in lieu of the required heat treatment after welding, bending, or forming, provided that the mechanical properties of any affected weld and base metal meet specification requirements after such treatment and that the substitution is approved by the designer.

12.1.7 Exceptions to Basic Requirements

The basic practices therein may require modification to suit service conditions in some cases. In such cases, the designer may specify more stringent requirements in the engineering design, including heat treatment and hardness limitations for lesser thickness, or may specify less stringent heat treatment and hardness requirements, including none.

When provisions less stringent than those in Table 11.13 are specified, the designer must demonstrate to the owner's satisfaction the adequacy of those provisions by comparable service experience, considering service temperature and its effects, frequency and intensity of thermal cycling, flexibility stress levels, probability of brittle failure, and other pertinent factors. In addition, appropriate tests should be conducted, including Welding Procedure Specification (WPS) qualification tests.

12.1.8 Dissimilar Materials

Heat treatment of welded joints between dissimilar ferritic metals or between ferritic metals using dissimilar ferritic filler metal should be at the higher of the temperature ranges in Table 11.13 for the materials in the joint.

Heat treatment of welded joints including both ferritic and austenitic components, and filler metals should be as required for the ferritic material or materials unless otherwise specified in the engineering design.

12.1.9 Delayed Heat Treatment

If a weldment is allowed to cool prior to heat treatment, the rate of cooling should be controlled or other means should be used to prevent detrimental effects.

12.1.10 Partial Heat Treatment

When an entire structure assembly to be heat treated cannot be fitted into the furnace, it is permissible to heat treat in stages, provided there is at least (0.3 m) 1 ft overlap between successive heats, and that the parts of the assembly outside the furnace are protected from harmful temperature gradients.

12.1.11 Local Heat Treatment

When heat treatment is applied locally, a circumferential band of the run structure, and of the branch where applicable, should be heated until the specified temperature range exists over the entire section(s), gradually diminishing beyond the ends of a band that includes the weldment or the bent or formed section and at least 25 mm (1 inch) beyond the edges thereof.

12.1.12 Heat Treatment of Casing and Tubing

Furnished pipe should be made by the seamless or electric weld process as shown in Table 12.1. Pup joints and connectors may be made from standard casing or tubing, or by machining heavy wall casing, tubing, or bar stock. Couplings should be manufactured by one of the processes listed in Paragraph 8.1 of API, 5CT. Cold-drawn tubular products without appropriate heat treatment are not acceptable:

- Seamless pipe is defined as a wrought steel tubular product made without a welded seam. It is manufactured by hot working steel, or if necessary, by subsequently cold finishing the hot-worked tubular product to produce the desired shape, dimensions, and properties.
- Electric-welded pipe is defined as pipe having one longitudinal seam formed by electric-flash welding or electric-resistance welding, without the addition of extraneous metal. The weld seam of electric-welded pipe should be heat treated after welding to a minimum temperature of 538 °C (1000 °F), or processed in such a manner that no untempered martensite remains.

12.2 Heat Treatment Process

During the pipe manufacturing process, for prevention of stress corrosion, the pipe should be heat treated as stipulated in Table 12.1 for the particular grade and type specified by the purchaser.

Table 12.1 *Process of manufacture and heat treatment*

Group	Grade	Type	Process of manufacture*	Heat treatment	Tempering temperature, minimum
1	H40	–	S or EW	None	–
1	J55	–	S or EW	None	–
1	K55	–	S or EW	None	–
1	N80	–	S or EW	None	–
2	L80	1	S or EW	Quenched and tempered	566
2	L80	9Cr	S	Quenched and tempered	593
2	L80	13Cr	S	Quenched and tempered	593
2	C90	1	S	Quenched and tempered	621
2	C90	2	S	Quenched and tempered	621
2	C95	–	S or EW	Quenched and tempered	538
2	T95	1	S	Quenched and tempered	649
2	T95	2	S	Quenched and tempered	649
3	P110	–	S or EW	Quenched and tempered	–
4	Q125	1	S or EW	Quenched and tempered	–
4	Q125	2	S or EW	Quenched and tempered	–
4	Q125	3	S or EW	Quenched and tempered	–
4	Q125	4	S or EW	Quenched and tempered	–

Note:
Full length normalized, normalized and tempered (N & T), or quenched and tempered (Q & T), at the manufacturer's discretion or if so specified on the purchase order.
Type 9 Cr and 13 Cr grades may be air quenched.
Special requirements unique to electric welded Q-125 casing are specified in ISO 11960 SR12. When electric welded P110 or Q-125 casing is furnished, provisions of ISO 11960 SR11 are automatically in effect.
*S: Seamless; EW: Electric-welded

Heat treated upset pipe should be heat treated over the full length after upsetting. When requested by the purchaser, the manufacturer/processor should produce evidence to show that the tempering practice for Group 2 pipe will result in the pipe attaining the minimum tempering temperature. Pipe and coupling stock should be heat treated over the full length.

12.2.1 Heat Treatment of Stainless Steel

Improper heat treatment can produce deleterious changes in the micro-structure of stainless steels. The most troublesome problems are carbide precipitation (sensitization) and precipitation of various intermetallic phases, such as σ, χ, and laves (η).

12.2.1.1 Sensitization

Sensitization, or carbide precipitation at grain boundaries, can occur when austenitic stainless steels are heated for a period of time in the range of about 425 to 870 °C (800 to 1600 °F). Time at temperature will determine the amount of carbide precipitation. When the chromium carbides precipitate in grain boundaries, the area immediately adjacent is depleted of chromium.

When the precipitation is relatively continuous, the depletion renders the stainless steel susceptible to intergranular corrosion, which is the dissolution of the low-chromium layer or envelope surrounding each grain. Sensitization also lowers resistance to other forms of corrosion, such as pitting, crevice corrosion, and SCC.

Time–temperature–sensitization curves are available that provide guidance on avoiding sensitization and illustrate the effect of carbon content on this phenomenon. The curves shown in Figure 12.2 indicate that a Type 304 stainless steel with 0.062% C would have to cool below 595 °C (1100 °F) within about 5 min to avoid sensitization, but a Type 304L with 0.030% C can take about 20 h to cool below 480 °C (900 °F) without becoming sensitized. These curves are general guidelines and should be verified before they are applied to various types of stainless steel.

Another method of avoiding sensitization is to use stabilized steels. Such stainless steels contain titanium and/or niobium. These elements have an affinity for carbon and form carbides readily; this allows the chromium to remain in solution even during extremely long exposures to temperatures in the sensitizing range. Type 304L can avoid sensitization during a relatively brief exposure to welding, but it will be sensitized by long exposures.

Annealing is the only way to correct a sensitized stainless steel. Because different stainless steels require different temperatures, times, and quenching procedures, the user should contact the material supplier for such information. A number of tests can detect sensitization resulting from carbide precipitation in austenitic and ferritic stainless steels. The most widely used tests are described in ASTM Standards A 262 and A 763. More detailed information on sensitization of stainless steels can be found in various books on metallurgically influenced corrosion.

12.2.1.2 Precipitation of Intermetallic Phases

Sigma-phase precipitation and precipitation of other intermetallic phases also increases susceptibility to corrosion. Sigma phase is a chromium-molybdenum-rich phase that can render stainless steels susceptible to intergranular corrosion, pitting, and crevice corrosion. It generally occurs in higher-alloyed stainless steels (high-chromium, high-molybdenum stainless steels). Sigma phase can occur at a temperature range between 540 and 900 °C (1000 and 1650 °F). Like sensitization, it can be corrected by solution annealing.

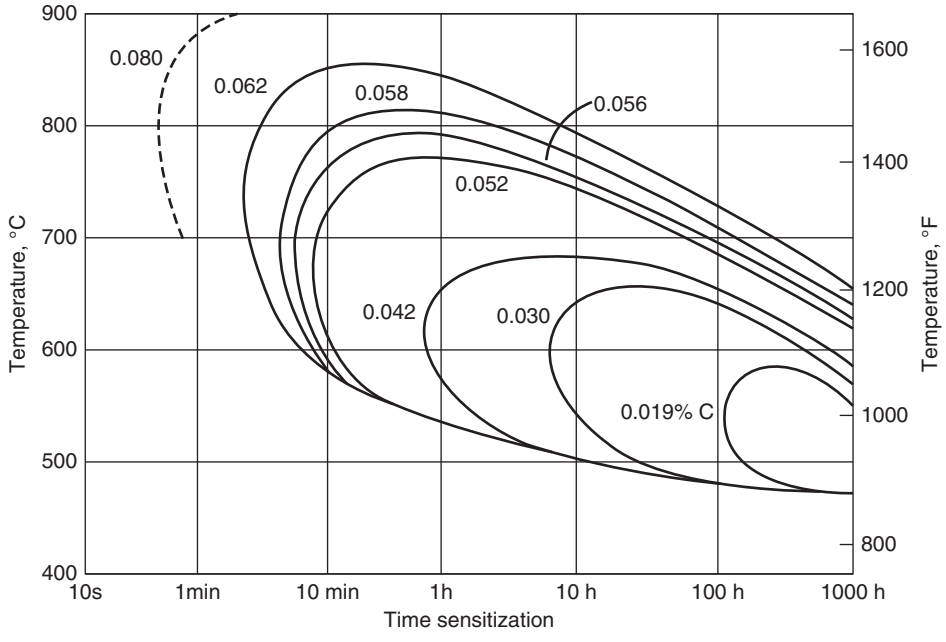


Figure 12.2 *Time–temperature–sensitization curves for Type 304 stainless steel in a mixture of $CuSO_4$ and H_2SO_4 containing free copper. Curves show the times required for carbide precipitation in steels with various carbon contents. Carbides precipitate in the areas to the right of the various carbon content curves. (Reproduced with permission from Daubert Cromwell.)*

12.2.1.3 Cleaning Procedures

Any heat treatment of stainless steel should be preceded and followed by cleaning. Steel should be cleaned before heat treating to remove any foreign material that may be incorporated into the surface during the high-temperature exposure. Carbonaceous materials on the surface could result in an increase in the carbon content, causing carbide precipitation. Salts could cause excessive intergranular oxidation. Therefore, the stainless steel must be clean before it is heat treated.

After heat treatment, unless an inert atmosphere was used during the process, the stainless steel surface will be covered with an oxide film. Such films are not very corrosion resistant and must be removed to allow the stainless steel to form its passive film and provide the corrosion resistance for which it was designed. There are numerous cleaning methods that may be used before and after heat treating. An excellent guide is ASTM A 380.

12.3 Preheating of Metals

Preheating is used, along with heat treatment, to minimize the detrimental effects of high temperature and severe thermal gradients inherent in welding. The necessity for preheating and the temperature to be used should be specified in the engineering design and demonstrated by procedure qualification.

The requirements and recommendations herein apply to all types of welding including tack welds, repair welds, and seal welds of threaded joints.

12.3.1 Requirements and Recommendations

Required and recommended minimum preheat temperatures for materials of various P-Nos. are given in Table 12.2. If the ambient temperature is below 0 °C (32 °F), the recommendations in Table 12.2 become requirements. The thickness intended in Table 12.2 is that of the thicker component measured at the joint.

12.3.1.1 Unlisted Materials

Preheat requirements for an unlisted material should be specified in the Welding Procedure Specification (WPS).

12.3.1.2 Temperature Verification

Preheat temperature should be checked by use of temperature indicating crayons, thermocouple pyrometers, or other suitable means to ensure that the temperature specified in the WPS is obtained prior to and maintained during welding.

Thermocouples may be temporarily attached directly to pressure containing parts using the capacitor discharge method of welding without welding procedure and performance qualifications. After thermocouples are removed, the areas should be visually examined for evidence of defects to be repaired.

12.3.1.3 Preheat Zone

The preheat zone should extend at least 25 mm (1 inch) beyond each edge of the weld.

12.3.2 Heat Treatment Specific Requirements

12.3.2.1 Dissimilar Materials

When materials having different preheat requirements are welded together, it is recommended that the higher temperature is used.

12.3.2.2 Interrupted Welding

If welding is interrupted, the rate of cooling should be controlled or other means should be used to prevent detrimental effects in the piping. The preheat specified in the WPS should be applied before welding is resumed.

For Cr-Mo steels, preheating in accordance with Appendix R of ASME Code Section VIII, and irrespective of wall thickness, should be carried out at the time of welding. This also applies to welding of nozzles, attachments, temporary brackets, and miscellaneous supports, temperatures should be checked and monitored.

A preheating as above should also be performed for carbon steel of large thickness (such as above 40 mm), for high-strength steel of medium thickness (such as above 25 mm).

When the required preheat temperature is 144 °C or higher, the temperature should be maintained at preheat temperature until the weld is completed.

Table 12.2 *Preheat temperatures*

Base metal P-No.*	Weld metal analysis A.No.**	Base-metal group	Nominal wall thickness		Specified min. tensile strength base metal		Min. temperature			
							Req.		Rec.	
			mm	m	Mpa	Ksi(s)	°C	°F	°C	°F
			< 25.4	< 1	≤ 490	≤ 71	–	–	10	50
1	1	Carbon steel	≥ 25.4	≥ 1	All	All	–	–	79	175
			All	All	> 490	> 71	–	–	79	175
			< 12.7	< 0.5	≤ 490	≤ 71	–	–	20	50
3	2.22	Alloy steels	≥ 12.7	≥ 0.5	All	All	–	–	79	175
		Cr s ½%	All	All	> 490	> 71	–	–	79	175
4	3	½% < Cr ≤ 2%	All	All	All	All	149	300	–	–
5	4.5	Alloy steels 2.14 ≤ Cr ≤ 10%	All	All	All	All	177	350	–	–
–	6	High-alloy steels, martansitic	All	All	All	All	–	–	149	300
7	7	High-alloy steels, ferritic	All	All	All	All	–	–	10	50
8	8,9	High-alloy steels, austanistic	All	All	All	All	–	–	10	50
9A,9B	10	Nickel alloy steels	All	All	All	All	–	–	95	200
10	–	Cr-Cu steel	All	All	All	All	149–204	300–400	–	–
10A	–	Mn-V steel	All	All	All	All	–	–	79	175
10E	–	27 Cr steel	All	All	All	All	149	300	–	–
11A SG1	–	8Ni, 9Ni steel	All	All	All	All	–	–	20	50
11A SG2	–	5 Ni steel	All	All	All	All	10	50	–	–
21-52	–	–	All	All	All	All	–	–	10	50

*P-Number from Boiler and Pressure Vessel Code (BPV) Section IX, Table QW-422 of ASME. Special P-Numbers (SP-1, SP-2, SP-3, SP-4, and SP-5) require special consideration. The required thermal treatment for Special P-Numbers should be established by the engineering design and demonstrated by the welding procedure qualification.
**A-Number from BPV Code, Section IX, QW-442

12.4 Surface Treatment of Stainless Steel

12.4.1 Surface Condition

To ensure satisfactory service life, the surface condition of stainless steels must be given careful attention. Smooth surfaces, as well as freedom from surface imperfections, blemishes, and traces of scale, and other foreign material, reduce the probability of corrosion. In general, a smooth, highly polished, reflective surface has greater resistance to corrosion. Rough surfaces are more likely to catch dust, salts, and moisture, which tend to initiate localized corrosive attack.

Oil and grease can be removed by using hydrocarbon solvents or alkaline cleaners, but these cleaners must be removed before heat treatment. Hydrochloric acid (HCl) formed from residual amounts of trichloroethylene, which is used for degreasing, has caused severe attack of stainless steels.

Surface contamination may be caused by machining, shearing, and drawing operations. Small particles of metal from tools become embedded in the steel surface and, unless removed, may cause localized galvanic corrosion. These particles are best removed by the passivation treatments described below. Additional information on cleaning and descaling of stainless steel is available in Volume 5 of the 9th Edition of *Metals Handbook*.

Shot-blasting or sand-blasting should be avoided unless iron-free silica is used; metal shot, in particular, will contaminate the stainless steel surface. If shot-blasting or shot-peening with metal grit is unavoidable, the parts must be cleaned after blasting or peening by immersing them in an HNO_3 solution, as noted above.

12.4.2 Passivation Techniques

During handling and processing operations, such as machining, forming, tumbling, and lapping, particles of iron, tool steel, or shop dirt may be embedded in or smeared on the surfaces of stainless steel components.

These contaminants may reduce the effectiveness of the natural oxide (passive) film that forms on stainless steels exposed to oxygen at low temperatures. If allowed to remain, these particles may corrode and produce rust-like spots on the stainless steel. To prevent this condition, semi-finished or finished parts are given a passivation treatment. This treatment consists of cleaning and then immersing stainless steel parts in a solution of HNO_3 or of HNO_3 plus oxidizing salts. The treatment dissolves the embedded or smeared iron, restores the original corrosion-resistant surface, and maximizes the inherent corrosion resistance of the stainless steel.

12.4.3 Cleaning

Each work piece to be passivated must be cleaned thoroughly to remove grease, coolant, or other shop debris. A worker will sometimes eliminate the cleaning step based on the reasoning that the cleaning and passivation of a grease-laden part will occur simultaneously by immersing it in an HNO_3 bath. This assumption is mistaken. The grease will react with the HNO_3 to form gas bubbles, which collect on the surface of the work piece and interfere with passivation.

Also, contamination of the passivating solution (particularly with high levels of chlorides) can cause flash attack, which results in a gray or black appearance and deterioration of the surface.

To avoid such problems, each part should be wiped clean of any large machining chips or other debris. More tenacious deposits should be removed by brushing with a stainless steel wire brush, grinding, polishing with an iron-free abrasive, or sand-blasting. Tools and materials used for these processes should be clean and used only for stainless steels. Machining, forming, or grinding oils must be removed in order for passivation to be effective.

Cleaning should begin with solvent cleaning, which may be followed by alkaline soak cleaning and thorough water rinsing. Optimum results are obtained in passivation when the parts to be treated are as clean as they would have to be for plating. When large parts or bulky vessels are to be cleaned, it may be necessary to apply cleaning liquids by means of pressure spray; exterior surfaces may be cleaned by immersion or swabbing.

12.4.4 Passivating

After cleaning, the work piece can be immersed in the passivating acid bath. As shown in Table 12.3, the composition of the acid batch depends on the grade of stainless steel. The 300 series stainless steels can be passivated in 20 vol% HNO_3. A sodium dichromate ($Na_2Cr_2O_7.2H_2O$) addition or an increased concentration of HNO_3 is used for less corrosion-resistant stainless steels to reduce the potential for flash attack.

The procedure suggested for passivating free-machining stainless steels is somewhat different from that used for non-free-machining grades. This is because sulfides of sulfur-bearing free-machining grades, which are totally or partially removed during passivation, create microscopic discontinuities in the surface of the machined part.

Even normally efficient water rinses can leave residual acid trapped in these discontinuities after passivation. This acid can then attack the surface of the part unless it is neutralized or removed. For this reason, a special passivation process, referred to as the alkaline–acid–alkaline method, is suggested for free-machining grades.

The following steps should be followed when passivating free-machining stainless steels with the alkaline–acid–alkaline technique:

- After degreasing, soak the parts for 30 min in 5 wt% sodium hydroxide (NaOH) at 70 to 80 °C (160 to 180 °F)
- Water rinse
- Immerse the part for 30 min in 20 vol% HNO_3 plus 22 g/L (3 oz/gal) $Na_2Cr_2O_7.2H_2O$ at 50 to 60 °C (120 to 140 °F)
- Water rinse
- Immerse for 30 min in 5 wt% NaOH at 70 to 80 °C (160 to 180 °F)
- Water rinse and dry.

12.4.5 Testing

Testing is often performed to evaluate the passivated surface. For example, 400 series, precipitation-hardening, and free-machining stainless steels are often tested in a cabinet capable of maintaining

Table 12.3 *Passivating solutions for stainless steels (non-free-machining grades)*

Grade	Passivation treatment
Austenitic 300 series grades Grades with 17% Cr (except 440 series)	20 vol% HNO_3 at 50–60 °C (120–140 °F) for 30 min
Straight chromium grades (12–14% Cr) High-carbon/high-chromium grades (440 series)	20 vol% HNO_3 plus 22 g/L (3 oz/gal) $Na_2Cr_2O_7.2H_2O$ at 50–60 °C (120–140 °F) for 30 min
Precipitation-hardening grades	50 vol% HNO_3 at 50–60 °C (120–140 °F) for 30 min

100% humidity at 35 °C (95 °F) for 24 h. Material that is properly passivated will be virtually free of rust, although light staining may occur. Austenitic 300 series grades can be evaluated using a technique given in ASTM Standard Method A 380. This test consists of swabbing the part with a copper sulfate ($CuSO_4.5H_2O$)/sulfuric acid (H_2SO_4) solution; wetness should be maintained for six min. Free iron, if present, plates out the copper from the solution, and the surface develops a copper cast or color. Information on passivation treatments for corrosion-resistant steels is also available in US Federal Specification QQ-P-35B.

12.5 Handling, Transport, Storage, and Erection of Coated Metalwork

12.5.1 Selection of Coating Systems

One of the factors that should be taken into account when selecting a coating system for a particular item is its resistance to mechanical damage during service. When works-coated steelwork is involved, the risk of damage to coatings during handling, transport, storage, and erection is greatly increased and the coating's resistance to mechanical damage assumes prime importance.

In addition to the risks of mechanical damage, coatings applied at works may also be subjected to many different adverse environments during transport and storage of steelwork before erection. Marine and other contaminating environments of various types, high humidity, and prolonged exposure for a variety of reasons may have to be allowed for. In some cases covers and other forms of protection may be provided prior to erection, but in most cases, the coating system should take these requirements into account in addition to fulfilling its role when in normal service.

Mechanical damage to coatings is of less consequence when only part of the system has been applied, because the making-good of damage to a full coating system is more difficult and costly, and may even be impossible where patch-painting of a final coat is not permitted. However, the adoption of a policy of partial coating at works and completion of the system at a later stage may lead to problems of intercoat contamination, and the resistance of the coating to the effects of adverse environments during transport and storage is reduced.

12.5.2 Methods of Preventing Damage

Care in the selection of coating systems will help to minimize damage to coatings before erection. Features that can be incorporated in the design of the fabrication and other measures that can be adopted to further reduce the effects of mechanical damage are as follows:

- The design should include lifting lugs or brackets where practicable
- The provision of a special lifting harness, nylon slings, rubber protected chains and chocks, etc.
- An adequate drying/curing period for each coat and for the complete system before handling
- Methods of loading that will reduce site handling to the minimum
- Order and timing of loading to reduce site storage to the minimum
- Special supports, packings, and lashings on the vehicles and trucks, and stacking in holds and on decks, to avoid chafing
- Special wrapping of coated pipes and packaging of smaller items.

12.5.3 Storage of Coated Steelwork

The degradation of coatings on stored steelwork can be minimized (especially in poor environments) by the adoption of the following precautions:

- Separators. Coated surfaces should preferably not be in contact. Wrapping, packaging, or crates used to reduce damage whilst items are in transit may perform this function. For large items, timber packings should be specified.
- Stacking. Components should be stacked in such a manner that there can be no section where cover is not provided. It may be necessary to limit the number of layers in a stack. The bottom layer should be laid on packing raised above the ground and the rain splash zone. Timber, usually of a softwood variety, provides a good surface on which coated steelwork may be stored with minimum damage to the coatings. Timber packing may be set on top of concrete or other more rigid supports. The area of the timber in contact with the members should be sufficiently large to avoid damage to the coatings, taking into account the dead weight of the steelwork stacked on the packing. The number of positions of the packing should ensure that steelwork is not distorted. Packing should be reasonably clean and free from any contaminating agents that may adversely affect coatings.

12.5.4 Responsibilities for Preventing Damage

The responsibilities for care of the coatings should be given careful consideration, since the benefits of careful coating work and handling whilst the items are at the works can be lost by rough treatment during transport to, or storage on, the site. The possible variations in the methods of transport and handling whilst steelwork is being moved and erected, and also in storage environments and other considerations, are limitless. It is not possible to give firm recommendations and the requirements for each project should be considered individually. It is essential, however, that the responsibilities at the design and erection stage are clearly defined and that decisions on coating systems, design requirements, methods of transport and handling, equipment used, and other special measures, are taken with a clear understanding of all requirements.

12.5.5 Transportation, Handling, and Storage of Coated Pipes

API RP5CI tubular goods in general, and threads in particular, are made with such precision that they require careful handling, and whether new, used, or reconditioned, they should always be handled with thread protectors in place.

12.5.5.1 Transportation

- Water transportation. Suppliers or their agents should provide proper supervision at the time of loading and unloading of water carriers to guard against improper or insufficient dunnage, inadequate bracing to prevent shifting during lurching of the ship, stowing in or adjacent to bilge water, injurious chemicals or other corrosive material, dragging pipe along the pile and permitting couplings or thread protectors to hook together or strike the edge of hatch opening or bump against the ship rail.
- Railroad transportation. When loading pipe on freight cars in addition to ICC (International Chamber of Commerce) requirements, wooden stringers should be provided across the bottom of the car to provide suitable support for pipes and to allow space for lifting, and also to keep pipes away from dirt. If the bottom of the car is uneven, the stringers should be rigidly shimmed so that their tops will be in the same plane. Stringers should not be placed under couplings or the upset part of pipe. The load should be tied down and properly bulkheaded to keep it from shifting.
- Truck transportation. The following precautions should be taken for truck transportation:
- Load pipe on bolsters and tie down with suitable chain at the bolsters. In hauling long pipe, an additional chain should be provided in the middle.

- Load pipe with all couplings on the same end of the truck.
- Care should be taken to prevent chafing of tool-joint shoulders on adjacent joints.
- Do not overload the truck to the point where there is any danger that the load cannot be delivered to its destination without unloading.
- After the load has been hauled a short distance, retighten load binding chains loosened as a result of the load settling.
- Handling. The following precautions should be observed in handling pipes:
- Before unloading, make sure that the thread protectors are tightly in place. The use of a spreader-bar with a choker-sling at each end is the recommended method of handling long pipes.
- Avoid rough handling that might dinge or dent the body of the pipe. Out-of-roundness will reduce collapse strength greatly.
- Do not unload the pipe by dropping. Unload one, two, or three lengths at a time, depending upon the number that can be fully controlled. When unloading by hand use rope slings. When rolling down skids roll the pipe parallel to the stack and do not allow it to gather momentum or to strike the ends because, even with protectors in place, there is a danger of damaging the threads.
- Stop each length before it reaches the preceding length, then push into place by hand.
- Storage. The following precautions are recommended for pipe storage:
- Do not pile pipes directly on the ground, rails, steel, or concrete floors. The first tier of pipes should be no less than 18 inch from the ground to keep moisture and dirt away.
- Pipes should rest on supports properly spaced to prevent bending of the pipe or damage to the threads. The stringers should lie in the same plane and be reasonably level, and should be supported by piers adequate to carry the full stack load without settling.
- Provide wooden strips as separators between successive layers of pipe so that no weight rests on the couplings. Use at least three spacing strips.
- Place spacing strips at right angles to the pipes and directly above the lower strips and supports to prevent bending of the pipe.
- Stagger adjoining lengths of pipe in the tiers an amount approximating the length of the coupling.
- Block pipes by nailing 1×2 or 2×2 blocks at both ends of the spacing strips.
- For purposes of safety, ease of inspection, and handling, pipes should not be stacked higher than 3 m (10 ft.), or more than five tiers at the rig.
- Pipes in storage should be inspected periodically and protective coatings applied when necessary to arrest corrosion.

12.5.6 Handling and Storage of Aluminium

Because of the excellent corrosion resistance of the 1000, 3000, 4000, 5000, and 6000 series alloys, users occasionally have not employed good practice in the handling and storage of these alloys. This can result in water stains or in pitting. Methods to avoid these unsightly surface effects are described in the chapter "Cleaning and Finishing of Aluminium and Aluminium Alloys" in Volume 5 of the 9th Edition of *Metals Handbook*.

Water stain is superficial corrosion that occurs when sheets of bare metal are stacked or nested in the presence of moisture. The source of moisture may be condensation from the atmosphere that forms on the edges of the stack and is drawn between the sheets by capillary action. Aluminium should not be stored at temperatures or under atmospheric conditions conducive to condensation. When such conditions cannot be avoided, the metal sheets or parts should be separated and coated with oil or a suitable corrosion inhibitor. Once formed, water stain can be removed by either mechanical or chemical means, but the original surface brightness may be altered.

Outdoor storage of aluminium, even under a tarpaulin, is generally not desirable for long periods of time; this varies with the alloy, the end product, and the local environment. Moisture can collect on the surface, sometimes at relative humidities below the dew point, because of the hygroscopic nature of the dust or particles that deposit on the metal from the atmosphere.

The resulting staining or localized pitting, although of little structural consequence in the 1000, 3000, 4000, 5000, and 6000 alloys, is undesirable if the aluminium will be used for an end product for which surface finish is critical. The 2000 and 7000 bare alloys are susceptible to intergranular attack under these conditions, and for these alloys, use of strippable coatings, protective wrappers, papers, or inhibited organic films is advisable when adverse conditions cannot be avoided.

Mechanical damage can be easily avoided by good housekeeping practices, proper equipment, and proper protection during transportation. When transporting flat sheets or plates, the aluminium should be oiled or interleaved with approved paper to prevent traffic marks, where fretting action at points of contact causes surface abrasion.

12.6 Inspection

12.6.1 Importance of Inspection

Excellent materials selection, design, and detailed specification for construction of a plant or a piece of equipment may be set forth, but they can be essentially meaningless if they are not followed. Proper inspection is a must – particularly for critical components operating under hazardous conditions. Inspectors should scrutinize critically during fabrication and construction, not limiting inspection to the final product only. In addition to being capable and well qualified, inspectors should have substantial authority. Inspectional aspects are as important as design and material selection.

12.6.2 Results of a Lack of Good Inspection

Many examples of premature and sometimes catastrophic failures are known, as follows:

- A section of welded 254 mm (10 inch) pipe failed because the weld penetration at the joint was only 1.6 mm (1/16 inch) (merely an overlay). Incomplete weld penetration is not uncommon.
- Tube hungers in an oil refinery furnace failed because these castings were extremely porous (over 50% of the cross section at the point of fracture consisted of voids).
- Unsatisfactory performance was obtained because cleaning procedures were not followed.
- Cladding metal did not bond to the substrate steel because paper labels on the inner surface of the cladding were not removed.
- Rapid corrosion of heat exchanger tubing resulted because Type 304 stainless steel was used instead of the specified Type 316 stainless steel.
- Stress corrosion and/or fatigue failures because the radii at fillets were sharp instead of rounded, as called for on the drawings.
- Pressure tests must be properly executed.
- Many cases of improper heat treatment exist.
- Improper assembly, such as cold or hot bending of pipe to proper alignment induces high stresses and other undesirable factors.
- The wrong welding rod is sometimes used.
- Poor surface preparation results in failure of coatings.
- It was found that adequate inspection translates into good quality control.

12.7 Corrosion of Carbon Steel Weldments

12.7.1 SCC in Oil Refineries

Monoethanolamine (MEA) is an absorbent used to remove acid gases containing H_2S and CO_2 in oil-refining operations. Recent failures in several refineries have shown that cracks can be parallel or normal to welds, depending on the orientation of principal tensile stresses. Cracking has been reported to be both transgranular and intergranular.

Before 1978, postweld stress relief of carbon steel weldments in MEA systems was performed only when the metal temperature of the equipment was expected to exceed 65 °C (150 °F) and the acid gas contained more than 80% CO_2, or when temperatures were expected to exceed 95 °C (200 °F) in any acid gas concentration.

Currently, any equipment containing MEA at any temperature and at any acid gas concentration is being postweld stress relieved. This is the result of surveys conducted by several refineries to define the extent of the SCC problem in this environment. These inspection programs showed that leaks were widespread and were found in vessels that ranged in age from 2 to 25 years. However, there were no reports of cracking in vessels that had been postweld stress relieved. In addition, it was found that all concentrations of MEA were involved and that MEA solutions were usually at relatively low temperatures (below 55 °C, or 130 °F). Equipment found to suffer from cracking included tanks, absorbers, carbon treater drums, skimming drums, and piping. The following example of a metallurgical investigation conducted by one oil refinery illustrates the problem of SCC of carbon steel in amine service.

12.7.2 Leaking Carbon Steel Weldments in a Sulfur Recovery Unit

In December 1983, two leaks were discovered at a sulfur recovery unit. More specifically, the leaks were at pipe-to-elbow welds in a 152 mm (6 inch) diameter line operating in lean amine service at 50 °C (120 °F) and 2.9 MPa (425 psig). Thickness measurements indicated negligible loss of metal in the affected areas, and the leaks were clamped. In March 1984, 15 additional leaks were discovered, again at pipe-to-elbow welds of lean amine lines leading to two major refining units. The piping had been in service for about eight years.

12.7.2.1 Investigation

Metallurgical examination of several of the welds revealed that leaking occurred at what appeared to be stress-corrosion cracks originating from the inside surface. Cracks were present in weld metal and base metal approximately 5 mm (0.2 inch) away from the weld, and they passed through the HAZ, as shown in Figure 12.3.

In other cases, stress-corrosion cracks also originated in the HAZ. The cracks typically ran parallel to the weld (Figure 12.4).

Brinell hardness values, obtained by conversion of Knoop micro-hardness readings, were 133 to 160 (pipe base metal), 160 to 230 (weld metal), 182 to 227 (HAZs), and 117 to 198 (elbow base metal). The pipe base metal had an equiaxed fine-grain micro-structure typical of low-carbon steel, and the elbow base metal had a non-equiaxed micro-structure typical of hot-finished fittings. Carbon contents ranged from 0.25 to 0.30% by weight. Cracking was intergranular.

The refinery operators immediately embarked on a program of visual inspection of all amine lines. As of June 1985, a total of 35 leaks in lean amine piping had been discovered. All leaks were at cracks in or around pipe-to-elbow welds, except for two leaks at welds that connected a tee and a reducer, respectively. Piping size ranged from 76 to 305 mm (3 to 12 inches).

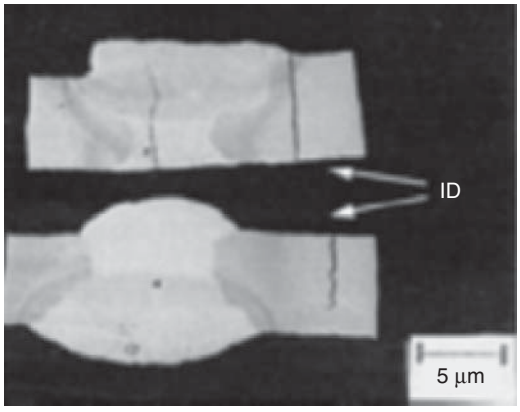


Figure 12.3 *Cross sections of pipe-to-elbow welds showing stress-corrosion cracks originating from the inside surface of the weld metal and the base metal.*

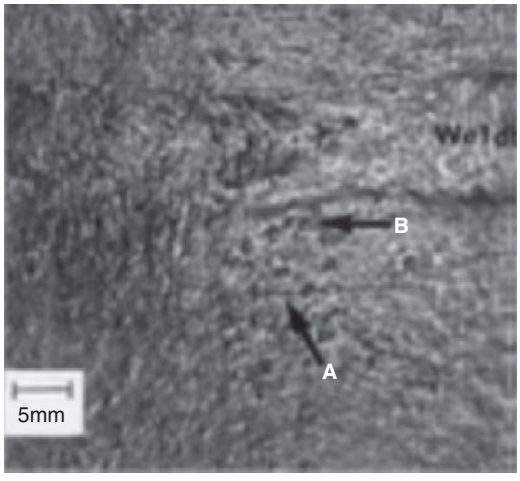


Figure 12.4 *Photograph of the inside surface of a pipe showing a 38 mm (1.5 inch) stress corrosion crack (A) next to and parallel to a circumferential weld. Also shown are shoulder corrosion pits (B).*

Service temperature ranged from 40 to 60 °C (100 to 140 °F), with most leaks having occurred in lines carrying lean amine at 55 °C (130 °F). Pressures ranged from atmospheric to 2.9 MPa (425 psig), with most leaks having occurred between 2.8 and 2.9 MPa (400 and 425 psig). All piping had been in service for about eight years, except two leaks at piping welds that had been in service for only four years.

As had been generally accepted industry practice, the specifications called for stress relieving or postweld heat treatment of piping and vessels in amine service at temperatures above 95 °C (200 °F). Therefore it was highly unlikely that any of the leaking welds had received postweld heat treatment. Further metallurgical examination of leaking welds from various lines conclusively confirmed that the leaking originated at stress corrosion cracks. No leaks were found in rich amine piping. The characteristics of the mode of fracture suggested that the failure mechanism was a form of caustic SCC.

It is interesting to note that other researchers have also metallographically examined numerous samples of similar cracks; their results can be summarized as follows:

- Cracks were essentially intergranular and were filled with gray oxide scale
- Hardness of welds and HAZs was less than 200 HB
- Cause of fracture was believed to be a form of caustic SCC
- Cracking occured whether or not MEA solutions contained corrosion inhibitors.

12.7.2.2 Preventive Measures

As a result of this particular investigation and others, all welds in equipment in MEA service are being inspected. Wet fluorescent magnetic-particle inspection after sand-blasting to remove oxides and scale appears to be the most effective technique. Shear-wave ultrasonic (SWU) inspection has also been used for piping, but it does not always distinguish SCC and other defect indications, such as shrinkage cracks, slag inclusions, lack of fusion, or fatigue cracks. Nevertheless, SWU is considered helpful, because these other types of defects can also pose a threat to the structural integrity of the system in question. Inspection frequency is dependent on the critical nature of the particular equipment in question, and most importantly, all welds in these systems are not being postweld stress relieved.

12.7.3 Corrosion of Welds in Carbon Steel Deaerator Tanks

Deaerator tanks, the vessels that control free oxygen and other dissolved gases to acceptable levels in boiler feed water, are subject to a great deal of corrosion and cracking. Several years ago, there were numerous incidences of deaerator tank failures that resulted in injury to personnel and property damage losses.

Since that time, organizations such as the National Board of Boiler and Pressure Vessel Inspectors and the Technical Association of the Pulp and Paper Industry have issued warnings to plant operators, and these have resulted in the formation of inspection programs for evaluating the integrity of deaerator tanks. As a result, many operators have discovered serious cracking problems. The following example illustrates the problem.

12.7.4 Weld Cracking in Oil-Refinery Deaerator Vessels

Two deaerator vessels with associated boiler feed-water storage tanks operated in similar service at a refinery. The vertical deaerator vessels were constructed of carbon steel (shell and dished heads), with trays, spray nozzles, and other internal components fabricated of Type 410 stainless steel.

Boiler feed water was treated by sand filtration using pressure filters, followed by ion-exchange water softening. Hardness was controlled at less than 0.5 ppm calcium carbonate ($CaCO_3$).

A strong cationic primary coagulant (amine) was used to aid the filtering of colloidal material. Treated water was blended with condensate containing 5 ppm of a filming amine corrosion inhibitor. The final chemistry of the feedwater was controlled to the limits given in Table 12.4. Oxygen scavenging was ensured by the addition of catalyzed sodium bisulfite ($NaHSO_3$) to the storage tanks. Treated water entered the top of the tray section of the deaerators through five or six spray nozzles and was stored in the horizontal tanks below the deaerators.

12.7.4.1 Inspection Results

Deaerator vessel and storage tank A were inspected. All tray sections were removed from the deaerator. With the exception of the top head-to-shell weld in the deaerator, all internal welds were ground smooth and magnetic particle inspected. No cracks were found.

Table 12.4 *Chemistry limits on deaerator feed water*

Control parameter	Limit
Total hardness	<0.5 ppm as $CaCO_3$
Phenolphthalein alkalinity	Trace (max.)
Methyl orange alkalinity	14–18 ppm as $CaCO_3$
Chloride	7.6–8.8 ppm
Total dissolved solids	70–125 ppm

Corrosion damage was limited to minor pitting of the bottom head in the deaerator vessel. Inspection of deaerator vessel B revealed cracking at one weld. Tray sections were removed from the deaerator vessel, and shell welds were grit-blasted. Except for the top head-to-shell weld in the deaerator, all internal welds in both B units were then ground smooth and magnetic particle inspected. Three transverse cracks were found at the bottom circumferential weld in the deaerator vessel. These were removed by grinding to a depth of 1.5 mm (0.06 inch).

Inspection of storage tank B revealed numerous cracks transverse to welds. With the shell constructed from three rings of plate, the longitudinal ring welds were located just below the water level. These longitudinal welds exhibited no detectable cracking. One circumferential crack was found above the working water level in the vessel. The remaining cracks were located at circumferential welds below the working water level. Numerous cracks transverse to circumferential welds were detected, but only one longitudinal crack was detected. All cracks were removed by grinding to a depth of 2 mm (0.08 inch).

Unlike deaerator vessel A, it was noted that none of the spray nozzles in deaerator vessel B was operational at the time of inspection. In addition, two valves had fallen to the bottom of the deaerator vessel. The bottom section of trays in deaerator vessel B had fallen to the bottom of the storage vessel. Corrosion damage in deaerator vessel B was limited to underdeposit pitting attack at circumferential welds in the bottom.

12.7.4.2 Metallurgical Analysis

A section was cut from a circumferential weld region in storage tank B. The cracking was predominantly transverse to the weld. Chemical analysis was performed on samples cut from weld metal and base metal; the results are given in Table 12.5 and show that the steel plate was not aluminium- or silicon-killed, but was most likely a rimmed grade. Cross sections were cut perpendicular to both transverse and longitudinal cracks and were examined metallographically.

Metallographic examination of the base-metal structures revealed ferrite and lamellar pearlite phases with a nearly equiaxed grain structure. The approximate grain size was ASTM 6 to 7. Figure 12.5 shows a longitudinal crack in a weld HAZ, with associated grain refinement. Cracking initiated from the bottom of a pit. The oxide associated with the major crack was extensive and

Table 12.5 *Chemical analyses of steels and weld deposit*

	Analysis, %									
Sample	C	Mn	Si	P	S	Ni	Cr	Mo	Al	Fe
Plate 1	0.25	0.88	<0.05	0.029	0.036	<0.05	<0.05	<0.03	<0.01	Balance
Plate 2	0.21	0.83	<0.05	0.03	0.024	<0.05	<0.05	<0.03	<0.01	Balance
Weld deposit	0.14	0.53	0.14	0.035	0.031	<0.05	<0.05	<0.03	<0.01	Balance

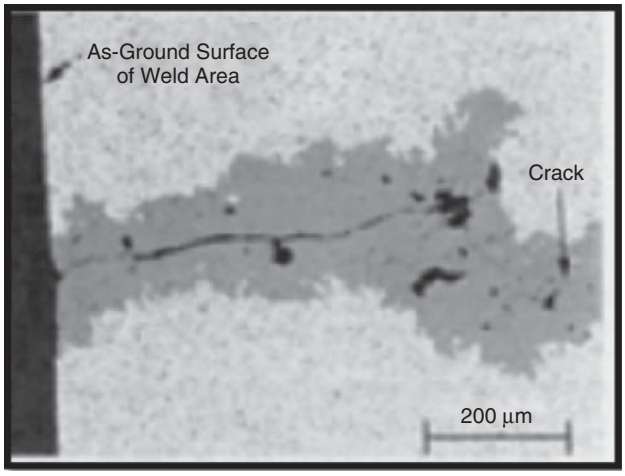


Figure 12.5 *Micrograph of a longitudinal crack in the HAZ of a weld from storage vessel B etched with nital.*

contained numerous secondary cracks. Analysis of the oxide deposit within the crack by wavelength-dispersive spectroscopy revealed slightly less oxygen than an Fe_2O_3 standard. Therefore, it was assumed that the oxide deposit was a mixture of Fe_3O_4 and Fe_2O_3.

Figure 12.6 shows a crack extending into base metal, transverse to the weld, with secondary cracking to the periphery of the oxidized region. It was clear that the oxide exhibited extensive internal cracking. The figure also shows the entrainment of a lamellar pearlite phase (dark) within the oxide corrosion product. In addition, the crack tips are blunt.

Discussion

The cracks described in this example are very similar to those found in many other investigations, despite a variety of deaerator vessel designs and operating conditions. Cracks typically display the following characteristics:

- Cracks occur most often in welds and HAZs, but can also occur in the base metal.
- Cracks are generally transverse to the weld HAZ, and occur both parallel and perpendicular to the hoop stress direction.
- The worst cracks appear to be located in circumferential and head-to-shell welds in horizontal vessel designs.
- Cracks are concentrated at, but not solely located within, the working water level in the vessel.
- Cracks are perpendicular to the vessel plate surface.
- Cracks are predominantly transgranular with minor amounts of branching.
- Cracks are filled with iron oxide. Cracking of the oxide corrosion product is followed by progressive corrosion.
- The ferrite phase is selectively attacked, with retention of the pearlite phase within the oxide corrosion product.
- Cracks initiate from corrosion pits. Weld defects, however, can also become active sites for crack initiation.
- Crack tips are blunt.

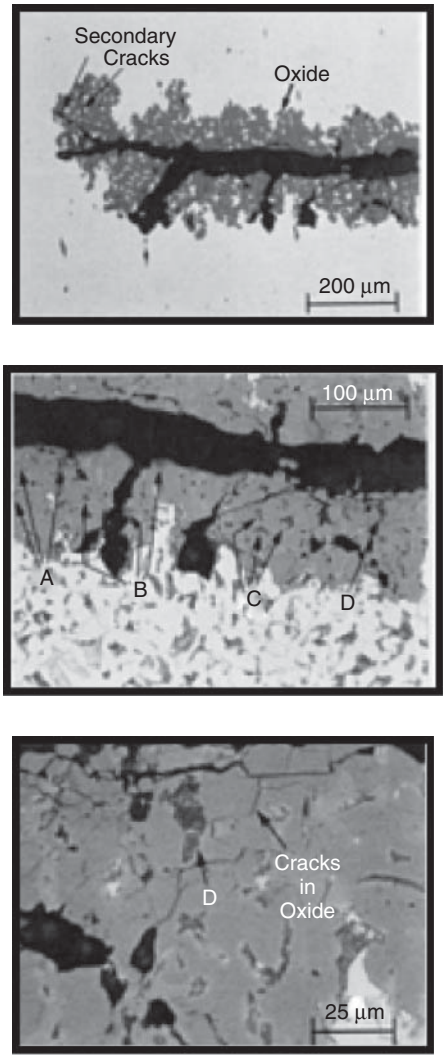


Figure 12.6 *Micrographs of a transverse crack in a storage vessel. (Top) Crack extending into base metal, as-polished. (Middle) Lamellar pearlite phase (dark) entrained in the oxide corrosion product. (Bottom) Micro-cracks and entrained pearlite phase in the oxide corrosion product. (Reproduced with permission from Daubert Cromwell.)*

Conclusions

These findings suggest that the failure mechanism is a combination of low-cycle corrosion fatigue and stress-induced corrosion. Extensive oxide formation relative to the depth of cracking is a key feature. The formation of oxide was associated with corrosion attack of the ferrite phase. The lamellar pearlite phase remained relatively intact and was contained within the oxide product. The oxide itself exhibited numerous cracks, allowing aqueous corrosion of fresh metal to occur at the oxide/metal interface.

Mechanical or thermal stresses are most likely responsible for this network of cracks within the oxide product. The mechanism appears to be stress-assisted localized corrosion. Sharp, tight cracks were not found in fresh metal beyond the periphery of the oxide corrosion product. It therefore appears reasonable that cracking could have occurred subsequent to corrosion and within the brittle oxide.

Cracking at welds and HAZs suggests that residual weld shrinkage stresses play a major role. Welds in deaerator vessels typically have not been postweld stress relieved. It is not unusual to find residual welding stresses of yield strength magnitude. This problem can be aggravated by vessel design (high localized bending stresses around saddle supports that fluctuate with water level and are accelerated by operational upsets). No fault was found with the steel plate chemical composition or with welding consumables. There was no evidence of embrittlement or caustic SCC (that is, no branched intergranular cracks).

12.7.4.3 Recommendations

All welds in deaerator vessels should be postweld stress relieved. Operational upsets should be avoided, and water chemistry must be maintained within acceptable limits. This is especially true with regard to water oxygen levels, which should be kept low to minimize pitting corrosion.

12.8 Corrosion of Austenitic Stainless Steel Weldments

12.8.1 Effects of GTA Weld Shielding Gas Composition

The chromium in a stainless steel has a strong chemical affinity for oxygen and carbon. Weld pools formed by electric arc processes must be shielded from the atmosphere to prevent slag formation and oxidation, to maintain a stable arc, and to reduce contamination of the molten metal by the weld environment. Argon or argon plus helium gas mixtures are commonly used in GTA welding processes to create a barrier between the solidifying weld and the atmosphere. In other cases, nitrogen is commonly used as a backing gas to protect the backside of the root pass.

The composition of a shielding gas can be modified to improve the micro-structure and properties of GTA welds in austenitic stainless steels. More specifically, the use of argon mixed with small volumes of nitrogen (10 vol% N_2 or less) in a GTA welding process enhances the corrosion resistance of iron-chromium-nickel-molybdenum-nitrogen stainless alloys in oxidizing acid chloride solutions. In certain non-oxidizing solutions, argon-nitrogen shielding gas reduces the ferrite content of the weld metal, and influences its solidification behavior.

The nitrogen content of weld metal increases with the partial pressure of nitrogen in the GTA weld shielding gas. The increase in weld metal nitrogen content is greater when nitrogen is mixed with an oxidizing gas, such as CO_2, than with either a reducing (hydrogen) or a neutral (argon) gas. Porosity and concavity are observed in austenitic stainless steel weld metals when more than 10 vol% nitrogen is added to an argon shielding gas. Although solid-solution additions of nitrogen are not detrimental to the SCC resistance of unwelded molybdenum-containing austenitic stainless steels, an increased weld metal nitrogen content tends to increase susceptibility to SCC.

12.8.2 Effects of Heat-Tint Oxides on the Corrosion Resistance Of Austenitic Stainless Steels

Under certain laboratory conditions, a mechanically stable chromium-enriched oxide layer can be formed on a stainless steel surface that enhances corrosion resistance. In contrast, the conditions created by arc welding operations produce a scale composed of elements that have been selectively

oxidized from the base metal. The region near the surface of an oxidized stainless steel is depleted in one or more of the elements that have reacted with the surrounding atmosphere to form the scale.

The rate of oxidation for a stainless steel, and consequently the degree of depletion in the base metal, is independent of the alloy composition and is controlled by diffusion through the oxide. The oxidized, or heat-tinted, surface of a welded stainless steel consists of a heterogeneous oxide composed primarily of iron and chromium above a chromium-depleted layer of base metal. The properties of such a surface depend on:

- The time and temperature of the thermal exposure
- The composition of the atmosphere in contact with the hot metal surface
- The chemical composition of the base metal beneath the heat-tint oxide
- The physical condition of the surface (contamination, roughness, thermomechanical history) prior to heat tinting
- The adherence of the heat-tint oxide to the base metal.

The defects, internal stresses, and composition of the heat-tint oxide make it a poor barrier to any corrosive media that might initiate localized corrosion in the chromium-depleted layer of base metal.

The severity of localized corrosion at heat-tinted regions exposed to oxidizing chloride solutions is directly related to the temperature of the hot metal surface during welding. A heat-tint oxide on an austenitic stainless steel exposed to air first becomes obvious at approximately 400 °C (750 °F). As the surface temperature is increased, differently colored oxides develop that appear to be superimposed upon the oxides formed at lower temperatures (Table 12.6).

Dark blue heat-tint oxides are the most susceptible to localized corrosion. It should be noted that gas-shielded surfaces do not form the same distinctly colored oxides as surfaces exposed to air during welding, but gas-shielded surfaces can also be susceptible to preferential corrosion.

Whether a weld heat tint should be removed prior to service depends on the corrosion behavior of the given alloy when exposed to the particular environment in question. Preferential corrosion at heat-tinted regions is most likely to occur on an alloy that performs near the limit of its corrosion resistance in service, but certain solutions do not affect heat-tinted regions.

Even when heat-tinted regions are suspected of being susceptible to accelerated corrosion in a particular environment, the following factors should be considered:

- The rate at which pits, once initiated in the chromium-depleted surface layer, will propagate through sound base metal

Table 12.6 *Welding conditions and corrosion resistance of heat-tinted UNS 531726 stainless steel plate*

Welding conditions*				Corrosion test results**		
Heat input		Welding current, A	Centerline heat-tint color	Maximum pit depth		Number of pits on heat-tinted surface
kJ/mm	kJ/inch			mm	mils	
0.3	7.525	50	None	0.1	4	2
0.59	15.05	100	Straw	0.7	28	10
0.89	22.576	150	Rose	0.8	31	50
1.19	30.101	200	Blue	0.7	28	>70
1.48	37.626	250	White	0.9	35	>70

*Single-pass autogenous bead-on-plate GTA welds were made to heat tint the root surface of 6.4 mm (1/4 inch) -thick plate samples

**Duplicate coupons, each one with 25 × 51 mm (1 × 2 inch) heat-tinted surface, were exposed to 10% $FeCl_3$ solutions at 50 °C (120 °F). The weld face and edges of each coupon were covered with a protective coating

- The hazards associated with the penetration, due to localized corrosion, of a process unit
- The cost and effectiveness of an operation intended to repair a heat-tinted stainless steel surface.

The corrosion resistance of heat-tinted regions can be restored in three stages. First, the heat-tint oxide and chromium-depleted layer are removed by grinding or wire brushing. Second, the abraded surface is cleaned with an acid solution or a pickling paste (a mixture of HNO_3 and HF suspended in an inert paste or gel) to remove any surface contamination and to promote the reformation of a passive film. Third, after a sufficient contact time, the acid cleaning solution or pickling paste is thoroughly rinsed with water, preferably demineralized or with a low chloride ion (Cl^-) content.

Grinding or wire brushing may not be sufficient to repair a heat-tinted region. Such abrading operations may only smear the heat-tint oxide and embed the residual scale into the surface, expose the chromium-depleted layer beneath the heat-tint oxide, and contaminate the surface with ferrous particles that were picked up by the grinding wheel or wire brush.

A stainless steel surface should never be abraded with a wheel or brush that has been used on a carbon or low-alloy steel; wire brushes with bristles that are not made of a stainless steel of similar composition should also be avoided. Conversely, attempting to repair a heat-tinted region with only a pickling paste or acid solution may stain or even corrode the base metal if the solution is overly aggressive or is allowed to contact the surface for an extended time.

If the acid is too weak, a chromium-depleted scale residue may remain on a surface. Even if the chromium-depleted layer was completely removed by a grinding operation, mechanically ground surfaces generally have inferior corrosion resistance compared to properly acid-pickled surfaces.

12.8.3 Unmixed Zones

All methods of welding stainless steel with a filler metal produce a weld fusion boundary consisting of base metal that has been melted, but not mechanically mixed with filler metal and a partially melted zone in the base metal. The weld fusion boundary lies between a weld composite consisting of filler metal diluted by base metal and the HAZ in the base metal. The width of the unmixed zone depends on the local thermal conditions along the weld fusion line. For a GTA welding process, the zone is most narrow at the weld face and is broadest near the middle of the weld thickness.

An unmixed zone has the composition of base metal, but the micro-structure of an autogenous weld. The micro-segregation and precipitation phenomena characteristic of autogenous weldments decrease the corrosion resistance of an unmixed zone relative to the parent metal.

Unmixed zones bordering welds made from overalloyed filler metals can be preferentially attacked when exposed on the weldment surface.

The potential for preferential attack on unmixed zones can be reduced by minimizing the heat input to the weld and/or by flowing molten filler metal over the surface of the unmixed zone to form a barrier to the service environment.

Care must be taken in this latter operation to avoid cold laps and lack-of-fusion defects. In both cases, preferential attack is avoided as long as the surface of the unmixed zone lies beneath the exposed surface of the weldment.

12.8.4 Chloride SCC

Welds in the 300 series austenitic stainless steels, with the exception of Types 310 and 310-Mo, contain a small amount of ferrite (usually less than 10%) to prevent hot cracking during weld

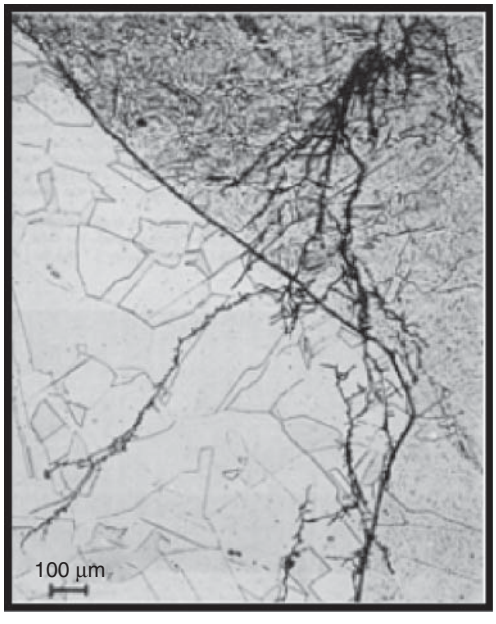


Figure 12.7 *Chloride SCC of Type 304 stainless steel base metal and Type 308 weld metal in an aqueous chloride environment at 95 °C (200 °F). Cracks are branching and transgranular. (Reproduced with permission from Daubert Cromwell.)*

solidification. In hot aqueous chloride environments, these duplex weldments generally show a marked resistance to cracking, while their counterparts crack readily.

The generally accepted explanation for this behavior is that the ferrite phase is resistant to chloride SCC and impedes crack propagation through the austenite phase. Electrochemical effects may also play a part; however, under sufficient tensile stress, temperature, and chloride concentration, these duplex weldments will readily crack. An example is shown in Figure 12.7.

12.8.5 Caustic Embrittlement (Caustic SCC)

Susceptibility of austenitic stainless steels to this form of corrosion usually becomes a problem when the caustic concentration exceeds approximately 25% and temperatures are above 100 °C (212 °F). Because welding is involved in most fabrications, the weld joint becomes the focus of attention because of potential stress-raising effects and because of high residual shrinkage stresses. Cracking occurs most often in the weld HAZ.

In one case, a Type 316L reactor vessel failed repeatedly by caustic SCC where the process fluids contained 50% sodium hydroxide (NaOH) at 105 °C (220 °F). Failure was restricted to the weld HAZ adjacent to bracket attachment welds used to hold a steam coil.

The stresses caused by the thermal expansion of the Nickel 200 steam coil at 1034 kPa (150 psig) aggravated the problem. Figure 12.8 shows the cracks in the weld HAZ to be branching and intergranular. Because it was not practical to reduce the operating temperature below the threshold temperature at which caustic SCC occurs, it was recommended that the vessel be weld overlayed with nickel or that the existing vessel be scrapped and a replacement fabricated from Nickel 200.



Figure 12.8 *Caustic SCC in the HAZ of a Type 316L stainless steel NaOH reactor vessel. Cracks are branching and intergranular.*

12.8.6 Microbiologically Induced Corrosion (MIC)

Microbiological corrosion in the process industries is most often found in three areas: cooling water systems, aqueous waste treatment, and groundwater left in new equipment or piping systems after testing. Nearly all confirmed cases of MIC have been accompanied by characteristic deposits. These are usually discrete mounds. Deposit color can also be an indication of the types of micro-organisms that are active in the system. For example, iron bacteria deposits on stainless steel, such as those produced by *Gallionella*, are often reddish.

Investigators have shown that in almost all cases the environment causing the damage was natural, essentially untreated water containing one or more culprit species of microbiological organisms. In the case of austenitic stainless steel weldments, corrosion generated by bacteria takes a distinctive form, that is, sub-surface cavities with only minute pinhole penetration at the surface.

12.9 Corrosion of Ferritic Stainless Steel Weldments

12.9.1 Leaking Welds in a Ferritic Stainless Steel Wastewater Vaporizer

A nozzle in a wastewater vaporizer began leaking after approximately three years of service with acetic and formic acid wastewater at 105 °C (225 °F) and 414 kPa (60 psig).

12.9.1.1 Investigation

The shell of the vessel was weld fabricated in 1972 from 6.4 mm (1/4 inch) E-Brite stainless steel plate. The shell measured 1.5 m (58 inches) in diameter and 8.5 m (28 ft) in length. Non-destructive

examination included 100% radiography, dye-penetrant inspection, and hydrostatic testing of all E-Brite welds.

An internal inspection of the vessel revealed that portions of the circumferential and longitudinal seam welds, in addition to the leaking nozzle weld, displayed intergranular corrosion. At the point of leakage, there was a small intergranular crack.

The evidence indicated weldment contamination; therefore, effort was directed at finding the levels of carbon, nitrogen, and oxygen in the various components present before and after welding. The averaged results were as follows:

- E-Brite, stainless steel plate
  - Base plate
    - **C** = 6 ppm
    - **N** = 108 ppm (C + N = 114 ppm)
    - **O** = 57 ppm
  - Corroded longitudinal weld
    - **C** = 133 ppm
    - **N** = 328 ppm (C + N = 461 ppm)
    - **O** = 262 ppm
  - Corroded circumferential weld
    - **C** = 34 ppm
    - **N** = 169 ppm (C + N = 203 ppm)
    - **O** = 225 ppm
- E-Brite
  - Weld wire
    - **C** = 3 ppm
    - **N** = 53 ppm (C + N = 56 ppm)
    - **O** = 55 ppm
  - Sound longitudinal weld
    - **C** = 10 ppm
    - **N** = 124 ppm (C + N = 134 ppm)
    - **O** = 188 ppm
  - Sound circumferential weld
    - **C** = 20 ppm
    - **N** = 106 ppm (C + N = 126 ppm)
    - **O** = 85 ppm

These results confirmed suspicions that failure was due to excessive amounts of nitrogen, carbon, and oxygen. To characterize the condition of the vessel further, Charpy V-notch impact tests were run on the unaffected base metal, the HAZ, and the uncorroded (sound) weld metal. These tests gave the data in Table 12.7 for ductile-to-brittle transition temperatures.

Table 12.7 *Ductile-to-brittle transition*

Specimen	Temperature °C	Temperature °F
Base metal	40 ± 3	105 ± 5
HAZ	85 ± 3	180 ± 5
Weld	5 ± 3	40 ± 5

Comparison of the interstitial levels of the corroded welds, sound welds, base metal, and filler wire suggested that insufficient joint preparation (carbon pick-up) and faulty gas shielding were probably the main contributing factors that caused this weld corrosion failure. Discussions with the vendor uncovered two discrepancies.

First, the welder was using a large, 19 mm (¾ inch) inside diameter ceramic nozzle with a gas lens, but was flowing only 19 L/min (40 ft^3/h) of argon; this was the flow rate previously used with a 13 mm (½ inch) inside diameter gas lens nozzle.

Second, a manifold system was used to distribute pure argon welding gas from a large liquid argon tank to various satellite welding stations in the welding shop. The exact cause for the carbon pick-up was not determined.

12.9.1.2 Conclusions

Failure of the nozzle weld was the result of intergranular corrosion caused by the pick-up of interstitial elements and subsequent precipitation of chromium carbides and nitrides. Carbon pick-up was believed to have been caused by inadequate joint cleaning prior to welding. The increase in the weld nitrogen level was a direct result of inadequate argon gas shielding of the molten weld puddle. Two areas of inadequate shielding were identified:

- Improper gas flow rate for a 19 mm (¾ inch) diameter gas lens nozzle
- Contamination of the manifold gas system.

In order to preserve the structural integrity and corrosion performance of the new generation of ferritic stainless steels, it is important to avoid the pickup of the interstitial elements carbon, nitrogen, oxygen, and hydrogen. In this particular case, the vendor used a flow rate intended for a smaller welding torch nozzle.

The metal supplier recommended a flow rate of 23 to 28 L/min (50 to 60 ft^3/min) of argon for a 19 mm (¾ inch) gas lens nozzle. The gas lens collect body is an important and necessary part of the torch used to weld these alloys. Failure to use a gas lens will result in a flow condition that is turbulent enough to aspirate air into the gas stream, thus contaminating the weld and destroying its mechanical and corrosion properties.

The manifold gas system also contributed to this failure. When this system is first used, it is necessary to purge the contents of the manifold of any air to avoid oxidation and contamination. When that is done, the system functions satisfactorily; however, when it is shut down overnight or for repairs, air infiltrates back in, and a source of contamination is re-established. Manifold systems are never fully purged, and leaks are common.

The contaminated welds were removed, and the vessels were rewelded and put back into service. Some rework involved the use of covered electrodes of dissimilar composition. No problems have been reported to date.

12.9.1.3 Recommendations

First, to ensure proper joint cleaning, solvent washing and wiping with a clean lint-free cloth should be performed immediately before welding. The filler wire should be wiped with a clean cloth just prior

to welding. Also, a word of caution: solvents are generally flammable and can be toxic. Ventilation should be adequate. Cleaning should continue until cloths are free of any residues.

Second, when GTA welding, a 19 mm (3/4 inch) diameter ceramic nozzle with gas lens collect body is recommended, an argon gas flow rate of 28 L/min (60 ft^3/h) is optimum. Smaller nozzles are not recommended. Argon back gas shielding is mandatory at a slight positive pressure to avoid disrupting the flow of the welding torch.

Third, the tip of the filler wire should be kept within the torch shielding gas envelope to avoid contamination and pickup of nitrogen and oxygen (they embrittle the weld). If the tip becomes contaminated, welding should be stopped, the contaminated weld area ground out, and the tip of the filler wire that has been oxidized should be snipped off before proceeding with welding.

Fourth, a manifold gas system should not be used to supply shielding and backing gas. Individual argon gas cylinders have been found to provide optimum performance. A weld button spot test should be performed to confirm the integrity of the argon cylinder and all hose connections. In this test, the weld button sample should be absolutely bright and shiny. Any cloudiness is an indication of contamination. It is necessary to check for leaks or replace the cylinder.

Fifth, it is important to remember that corrosion resistance is not the only criterion when evaluating these new ferritic stainless steels. Welds must also be tough and ductile, and these factors must be considered when fabricating welds.

Lastly, dissimilar weld filler metals can be successfully used. To avoid premature failure the dissimilar combination should be corrosion tested to ensure suitability for the intended service.

12.10 Corrosion of Duplex Stainless Steel Weldments

The influence of different welding conditions on various material properties of Alloy 2205 has been studied. Chemical compositions of test materials are given in Table 12.8, and the results of the investigation are detailed in the following sections.

12.10.1 Intergranular Corrosion

Despite the use of very high arc energies (0.5 to 6 kJ/mm, or 13 to 152 kJ/inch) in combination with multi-pass welding, the Strauss test (ASTM A 262, Practice E) failed to uncover any signs of sensitization after bending through 180°.

The results of Huey tests (ASTM A 262, Practice C) on submerged arc welds showed that the corrosion rate increased slightly with arc energy in the studied range of 0.5 to 6.0 kJ/mm (13 to 152 kJ/inch). For comparison, the corrosion rate for parent metal typically varies between 0.15 and 1.0 mm/y (6 and 40 mils/y), depending on surface finish and heat-treatment cycle.

Similar results were obtained in Huey tests of specimens from bead-on-tube welds produced by GTA welding. In this case, the corrosion rate had a tendency to increase slightly with arc energy up to 3 kJ/mm (76 kJ/inch).

12.10.2 Pitting Tests

Pitting tests were conducted in 10% ferric chloride ($FeCl_3$) at 25 and 30 °C (75 and 85 °F) in accordance with ASTM G 48. Results of tests on submerged arc test welds did not indicate any significant change in pitting resistance when the arc energy was increased from 1.5 to 6 kJ/mm (38 to 152 kJ/inch). Pitting occurred along the boundary between two adjacent weld beads. Attack was caused by slag entrapment in the weld; therefore, removal of slag is important.

Table 12.8 *Chemical compositions of Alloy 2205 specimens tested and filler metals used in UNS, S 31803*

Specimen size and configuration	Element, %									
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
Parent metals										
48.1 mm (1.89 inch) OD, 3.8 mm (0.149 inch) wall tube	0.015	0.37	1.54	0.024	0.003	21.84	5.63	2.95	0.09	0.15
88.9-mm (3.5 inch) OD, 3.6-mm (0.142 inch) wall tube	0.017	0.28	1.51	0.025	0.003	21.9	5.17	2.97	0.09	0.15
110- mm (4.3 inch) OD, 8-mm (0.31 inch) wall tube	0.027	0.34	1.57	0.027	0.003	21.96	5.62	2.98	0.09	0.13
213- mm (8.4 inch) OD, 18-mm (0.7 inch) wall tube	0.017	0.28	1.5	0.026	0.003	21.85	5.77	2.98	0.1	0.15
20- mm (3/4 inch) plate	0.019	0.39	1.8	0.032	0.003	22.62	5.81	2.84	–	0.13
Filler metals										
1.6 mm (0.063 inch) diameter rod	0.011	0.48	1.61	0.016	0.003	22.5	8	2.95	0.07	0.13
3.25 mm (0.127 inch) diameter covered electrode	0.02	1.01	0.82	0.024	0.011	23.1	10.4	3.06	–	0.13
4.0 mm (0.16 inch) diameter covered electrode	0.016	0.94	0.78	0.015	0.011	23	10.5	3.13	–	0.11

Gas tungsten arc weld test specimens (arc energies from 0.5 to 3 kJ/mm, or 13 to 76 kJ/inch) showed a marked improvement in pitting resistance with increasing arc energy. In order for duplicate specimens to pass the $FeCl_3$ test at 30 °C (85 °F), 3 kJ/mm (76 kJ/inch) of arc energy was required. At 25 °C (75 °F), at least 2 kJ/mm (51 kJ/inch) was required to achieve immunity. Welds made autogenously (no nickel enrichment) were somewhat inferior, but improvements were achieved by using higher arc energies.

For comparison with a different alloy, Figure 12.9 shows the effect of heat input on the corrosion resistance of Ferralium Alloy 255 welds made autogenously and tested in $FeCl_3$ at 15 °C (60 °F). Preferential corrosion of the ferrite phase is shown in Figure 12.10. In a different test, Ferralium Alloy 255 was welded autogenously and tested in a neutral chloride solution according to ASTM D 1141 at 60 to 100 °C (140 to 212 °F). In this case, preferential attack on the austenite phase was observed. An example is shown in Figure 12.11. Similar results would be expected for Alloy 2205.

A study of the Alloy 2205 weld micro-structures revealed why high arc energies were found to be beneficial to pitting resistance. Many investigations have indicated that the presence of chromium nitrides in the ferrite phase lowers the resistance to pitting of the weld metal and the HAZ in duplex stainless steels. In this study, both weld metal and HAZ produced by low arc energies contained an

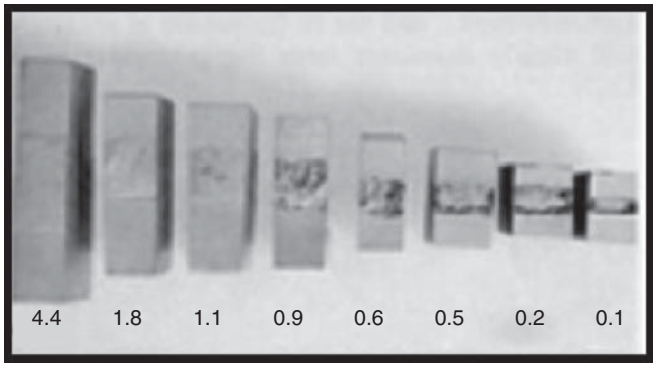


Figure 12.9 *Effect of welding heat input on the corrosion resistance of autogenous GTA (gas tungsten arc) welds in Ferralium Alloy 255 in 10% $FeCl_3$ at 10°C (40°F). The base metal was 25.4 mm (1 inch) thick.*

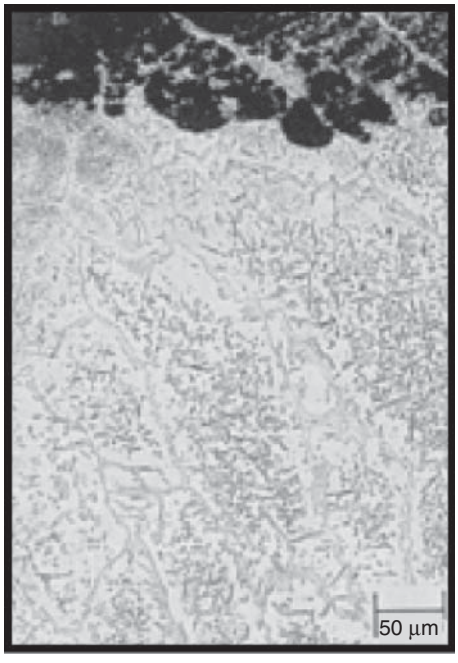


Figure 12.10 *Preferential corrosion of the ferrite phase in the weld metal of Ferralium Alloy 255 GTA welds in 10% $FeCl_3$ at room temperature. Base metal was 3.2 mm (1/8 inch) thick. (Reproduced with permission from Daubert Cromwell.)*

appreciable amount of chromium nitride (Cr_2N; Figure 12.12). The nitride precipitation vanished when an arc energy of 3 kJ/mm (76 kJ/inch) was used (Figure 12.13).

The results of $FeCl_3$ tests on submerged arc welds (SAW) showed that all top weld surfaces passed the test at 30 °C (85 °F) without pitting attack, irrespective of arc energy in the range of 2 to 6 kJ/mm (51 to 152 kJ/inch). Surprisingly, the weld metal on the root side, which was the first to be deposited, did not pass the same test temperature.

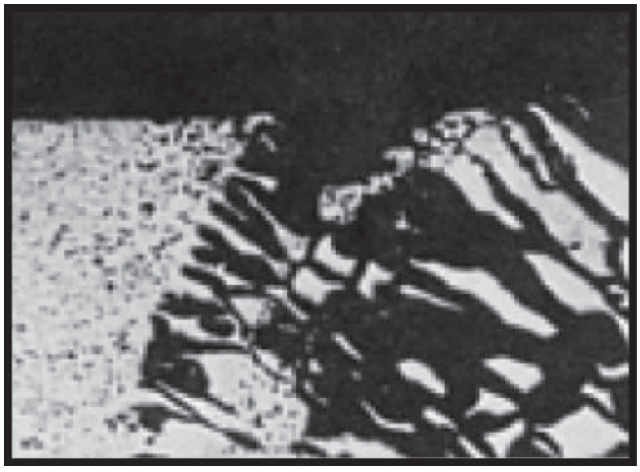


Figure 12.11 *Preferential attack of the continuous austenite phase in an autogenous GTA weld in Ferralium Alloy 255. Crevice corrosion test was performed in synthetic seawater according to ASTM D 1141 at 100°C (212°F). Etched with* 50% HNO_3 (×100). *(Reproduced with permission from Daubert Cromwell.)*

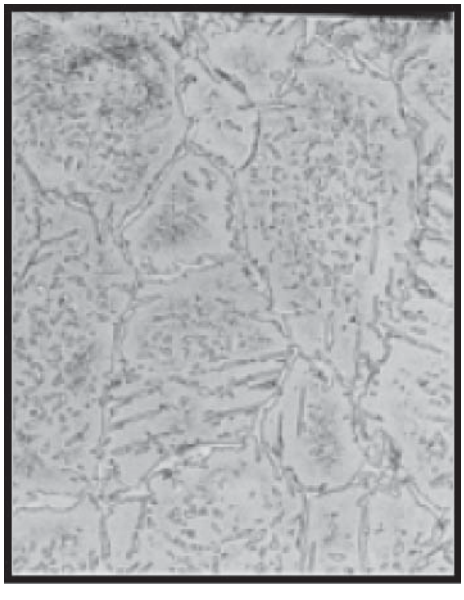


Figure 12.12 *Micro-structure of bead-on-tube weld made by autogenous GTA welding with an arc energy of 0.5 kJ/mm (13 kJ/inch). Note the abundance of chromium nitrides in the ferrite phase* (×200). *(Reproduced with permission from Daubert Cromwell.)*

The deteriorating effect of high arc energies on the pitting resistance of the weld metal on the root side was unexpected. Potentiostatic tests carried out in 3% NaCl at 400 mV versus SCE confirmed these findings. The higher the arc energy, the more austenite of this kind was present in the first two weld beads. Thus, nitrides give rise to negative effects on the pitting resistance, as do fine

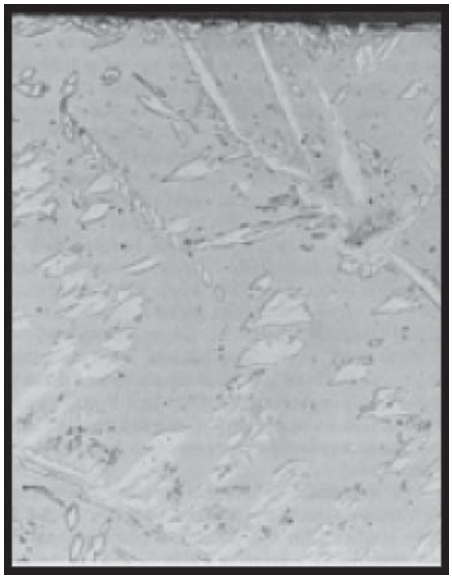


Figure 12.13 *Microstructure of bead-on-tube weld made by autogenous GTA welding with an arc energy of 3 kJ/mm (76 kJ/inch). Virtually no chromium nitrides are present, which results in adequate pitting resistance (×200). (Reproduced with permission from Daubert Cromwell.)*

austenite precipitates that were presumably reformed at as low a temperature as approximately 800 °C (1470 °F).

Therefore, the resistance of Alloy 2205 to pitting corrosion is dependent on several factors. First, Cr_2N precipitation in the coarse ferrite grains upon rapid cooling from temperatures above about 1200 °C (2190 °F) caused the most severe impairment to pitting resistance. This statement is supported by a great number of $FeCl_3$ tests, as well as by potentiostatic pitting tests.

Generally, it seems difficult to avoid Cr_2N precipitation in welded joints completely, particularly in the HAZ, the structure of which can be controlled only by the weld thermal cycle. From this point of view, it appears advisable to employ as high an arc energy as practical in each weld pass. In this way, the cooling rate will be slower (but not slow enough to encounter 475 °C (885 °F) embrittlement), and the reformation of austenite will clearly dominate over the precipitation of Cr_2N.

In addition, if there were no restriction on maximum interpass temperature, the heat produced by previous weld passes could be used to decrease the cooling rate further in the critical temperature range above about 1000 °C (1830 °F). Preliminary tests with preheated work pieces have shown the significance of temperature in suppressing Cr–N precipitation. Currently, the maximum recommended interpass temperature for Alloy 2205 is 150 °C (300 °F).

This temperature limit does not appear to be critical, and it is suggested that this limit could be increased to 300 °C (570 °F). The maximum recommended interpass temperature for Ferralium Alloy 255 is 200 °C (390 °F). Excessive grain growth as a result of too much heat input must also be considered to avoid loss of ductility and impact toughness.

Second, the fine austenite precipitates found in the reheated ferrite when high arc energies and multi-pass welding were combined are commonly referred to as $\gamma 2$ in the literature. The harmful influence of $\gamma 2$ on the pitting resistance has been noted with isothermally aged specimens, but as far as is known, it has never been observed in connection with welding. It is felt, however, that $\gamma 2$ is less

detrimental, with regard to pitting, than Cr_2N, Moreover, $\gamma 2$ formation is believed to be beneficial to mechanical properties, such as impact strength and ductility.

A third factor that lowers pitting resistance is oxide scale. Where possible, all surface oxides should be removed by mechanical means or, preferably, by pickling. Root surfaces (in pipe), however, are generally inaccessible, and pitting resistance must rely on the protection from the backing gas during GTA welding. It is therefore advisable to follow the current recommendation for stainless steels, which is a maximum of 25 ppm oxygen in the root backing gas.

12.11 Stress-Corrosion Cracking

The SCC resistance of Alloy 2205 in aerated, concentrated chloride solutions is very good. The effect of welding on the SCC resistance is negligible from a practical point of view. The threshold stress for various welds, as well as for unwelded parent metal in the $CaCl_2$ test, is as 90% of the tensile strength at the testing temperature. This is far above all conceivable design limits.

Also, in environments containing both hydrogen sulfide (H_2S) and chlorides, the resistance of welds is almost as high as for the parent metal. In this type of environment, however, it is important to avoid too high a ferrite content in the weld metal and HAZ. For normal welding of joints, the resulting ferrite contents should not cause any problems. For weld repair situations, however, care should be taken so that extremely high ferrite contents (>75%) are avoided. To preserve the high degree of resistance to SCC, the ferrite content should not be less than 25%.

Another reason to avoid coarse weld micro-structures (generated by excessive welding heat) is the resultant non-uniform plastic flow, which can locally increase stresses and induce preferential corrosion and cracking effects.

12.12 Use of High-Alloy Filler Metals

In critical pitting or crevice corrosion applications, the pitting resistance of the weld metal can be enhanced by the use of high nickel-chromium-molybdenum alloy filler metals. The corrosion resistance of such weldments in Ferralium Alloy 255 is shown in Table 12.9. For the same weld technique, it can be seen that using high-alloy fillers does improve corrosion resistance. If high-alloy fillers are used, the weld metal will have better corrosion resistance than the HAZ and the fusion line. Therefore, again, proper selection of welding technique can improve the corrosion resistance of the weldments.

12.13 Corrosion of Nickel-Bases Alloys

12.13.1 The Nickel–Molybdenum Alloys

Represented by Hastelloy Alloys B and B-2, nickel–molybdenum alloys have been primarily used for their resistance to corrosion in non-oxidizing environments such as HCl. Hastelloy Alloy B has been used since about 1929 and has suffered from one significant limitation: weld decay. The welded structure has shown high susceptibility to knifeline attack adjacent to the weld metal and to HAZ attack at some distance from the weld. The former has been attributed to the precipitation of molybdenum carbide (Mo_2C); the latter, to the formation of M_6C-type carbides. This necessitated postweld annealing, a serious shortcoming when large structures are involved. Many approaches to this problem

Table 12.9 *Corrosion resistance of Ferralium Alloy 255 weldments using various nickel-based alloy fillers and weld techniques; 3.2 mm (0.125 inch) plates tested in 10% $FeCl_3$ for 120 h*

Filler metal	Critical pitting temperature					
	Gas tungsten arc		As metal arc		Submerged arc	
	°C	°F	°C	°F	°C	°F
Hastelloy alloy G-3	30–35	85–95 (HAZ)	30	85 (HAZ)	30–35	85–95 (HAZ plus weld metal)
IN-112	30	85 (HAZ)	–	–	35–40	95–105 (HAZ plus weld metal)
Hastelloy alloy C-276	–	–	–	–	25–30	75–85 (HAZ)
Hastelloy alloy C-22	30	85 (HAZ)	–	–	35–40	95–105 (HAZ plus weld metal)

were attempted, including the addition of carbide-stabilizing elements, such as vanadium, titanium, zirconium, and tantalum, as well as the lowering of carbon level.

The addition of 1% V to an Alloy B-type composition was first patented in 1959. The resultant commercial alloys, Corronel 220 and Hastelloy Alloy B-282 were found to be superior to Alloy B in resisting knifeline attack, but were not immune to it. In fact, it was demonstrated that the addition of 2% V decreased the corrosion resistance of the base metal in HCl solutions. During this time, improvements in melting techniques led to the development of a low-carbon, low-iron version of Alloy B called Alloy B-2. This alloy did not exhibit any propensity to knifeline attack.

Segregation of molybdenum in weld metal can be detrimental to corrosion resistance in some environments. In the case of boiling HCl solutions, the weld metal does not corrode preferentially. However, in $H_2SO_4 + HCl$ and $H_2SO_4 + H_3PO_4$ acid mixtures, preferential corrosion of as-welded Alloy B-2 has been observed. No knifeline or HAZ attack was noted in these tests. During solidification, the initial solid is poorer in molybdenum and therefore can corrode preferentially. In such cases, postweld annealing at 1120 °C (2050 °F) will be beneficial.

12.13.2 The Nickel–Chromium–Molybdenum Alloys

Represented by the Hastelloy C family of alloys and by Inconel 625, the nickel–chromium–molybdenum alloys have also undergone evolution because of the need to improve the corrosion resistance of weldments. Hastelloy Alloy C (UNS N10002) containing nominally 16% Cr, 16% Mo, 4% W, 0.04% C, and 0.5% Si had been in use for some time, but had required the use of postweld annealing to prevent preferential weld and HAZ attack. Many investigations were carried out on the nature of precipitates formed in Alloy C, and two main types of precipitates were identified. The first was a Ni_7Mo_6 intermetallic phase called μ, and the second consisted of carbides of the Mo_6C type. Other carbides of the $M_{23}C6$ and M_2C were also reported. Another type, an ordered Ni_2Cr-type precipitate, occured mainly at lower temperatures and after a long aging time; it is not of great concern from a welding viewpoint.

Both the intermetallic phases and the carbides are rich in molybdenum, tungsten, and chromium and therefore create adjacent areas of alloy depletion that can be selectively attacked. Carbide precipitation can be retarded considerably by lowering carbon and silicon; this is the principle behind Hastelloy Alloy C-276.

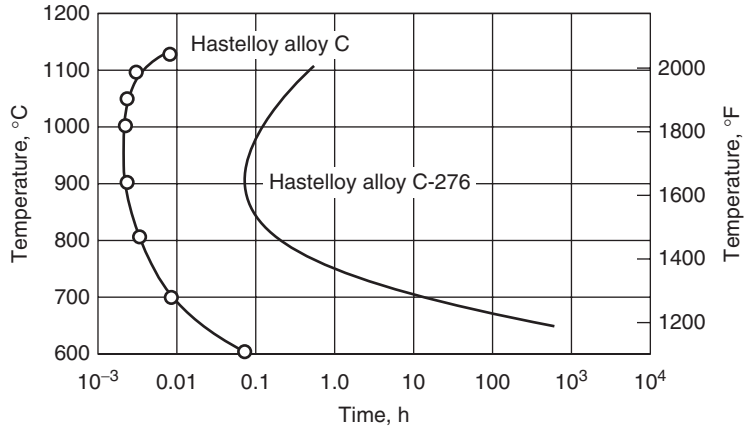


Figure 12.14 *Time–temperature transformation curves for Hastelloy Alloys C and C-276. Intermetallics and carbide phases precipitate in the regions to the right of the curves. (Reproduced with permission from Daubert Cromwell.)*

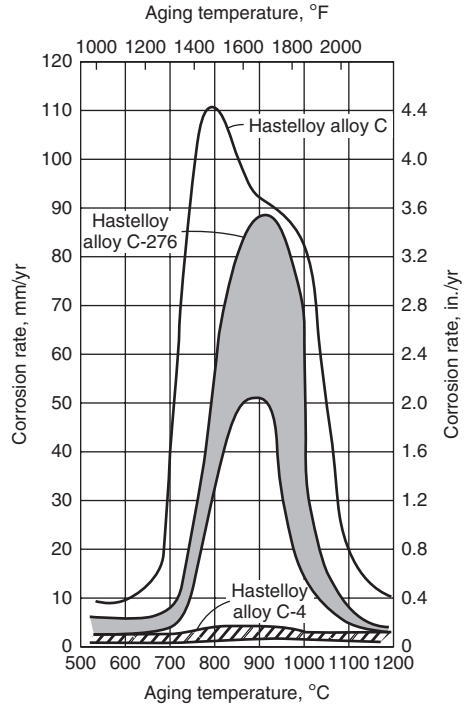


Figure 12.15 *Effect of 1 h aging treatment on corrosion resistance of three Hastelloy Alloys in 50% H_2SO_4 + 42 g/L $Fe_2(SO_4)_3$. (Reproduced with permission from Daubert Cromwell.)*

The time-temperature behaviors of Alloys C and C-276 are compared in Figure 12.14, which shows much slower precipitation kinetics in Alloy C-276. Therefore, the evolution of Alloy C-276 from Alloy C enabled the use of this alloy system in the as-welded condition. However, because only carbon and silicon were controlled in C-276, there remained the problem of intermetallic μ-phase precipitation, which occurred at longer times of aging. Alloy C-4 was developed with lower iron, cobalt, and tungsten levels to prevent precipitation of μ-μ-phases.

The effect of aging on sensitization of Alloys C, C-276, and C-4 is shown in Figure 12.15. For Alloy C, sensitization occurs in two temperature ranges (700 to 800 °C, or 1290 to 1470 °F, and 900 to 1100 °C, or 1650 to 2010 °F) corresponding to carbide and phase precipitation, respectively. For Alloy C-276, sensitization occurs essentially in the higher- temperature region because of μ-phase precipitation. Also, the phase precipitation kinetics in Alloy C-276 are slow enough not to cause sensitization problems in many high heat input weldments; however, precipitation can occur in the HAZ of Alloy C-276 welds.

Because C-4 has lower tungsten than C-276, it has lower pitting and crevice corrosion resistance, for which tungsten is beneficial. Therefore, an alternate solution to Alloy C-4 was needed in which both corrosion resistance and thermal stability are preserved. Hastelloy Alloy C-22 has demonstrated improved corrosion resistance and thermal stability.

Because of the low carbon content of Alloy C-22, the precipitation kinetics of carbides were slowed. Because Alloy C-22 has lower molybdenum and tungsten levels than Alloy C-276, μ-phase precipitation was also retarded.

From a weld HAZ point of view, this difference is reflected in lower grain-boundary precipitation even in a high heat input weld. The HAZ micro-structure of Alloy C-4 was similar to this.

Glossary of Terms

Abrasion
The removal of surface material from any solid through the frictional action of another solid, liquid or gas, or a combination thereof.

Absorption
A process in which molecules are taken up by and distributed throughout the body of a liquid or solid.

Acceleration corrosion test
Method designed to approximate, in a short time, the deteriorating effect under normal long-term service conditions.

Acicular ferrite
A highly sub-structured, non-equiaxed ferrite formed upon continuous cooling by a mixed diffusion and shear mode of transformation that begins at a temperature slightly higher than the transformation temperature range for upper bainite. It is distinguished from bainite in that it has a limited amount of carbon available; thus there is only a small amount of carbide present.

Acid
A substance that releases hydrogen ions when dissolved in water. Most acids will dissolve the common metals and will react with a base to form a neutral salt and water.

Acid embrittlement
A form of hydrogen embrittlement that may be induced in some metals by acid.

Acid rain
Atmospheric precipitation with a pH below 3.6 to 5.7. Burning of fossil fuels for heat and power is the major factor in the generation of oxides of nitrogen and sulfur, which are converted into nitric and sulfuric acids washed down in the rain. See also atmospheric corrosion.

Acrylic
Resin polymerized from acrylic acid, methacrylic acid, eaters of these acids, or acrylonitrile.

Activation
The changing of a passive surface of a metal to a chemically active state. Contrast with passivation.

Active
A state in which a metal tends to corrode (opposite of passive).

Corrosion and Materials Selection: A Guide for the Chemical and Petroleum Industries, First Edition. Alireza Bahadori.
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Active metal

A metal ready to corrode, or being corroded.

Active potential

The potential of a corroding material.

Activity

A measure of the chemical potential of a substance, where chemical potential is not equal to concentration, that allows mathematical relations equivalent to those for ideal systems to be used to correlate changes in an experimentally measured quantity with changes in chemical potential.

Activity (ion)

The ion concentration corrected for deviations from ideal behavior. Concentration multiplied by activity coefficient.

Activity coefficient

A characteristic quantity expressing the deviation of a solution from ideal thermodynamic behavior; often used in connection with electrolytes.

Addition agent

A substance added to a solution for the purpose of altering or controlling a process. Examples include wetting agents in acid pickles, brighteners, or anti-pitting agents in plating solutions, and inhibitors.

Additive

A substance added in a small amount, usually to a fluid, for a special purpose, such as to reduce friction, corrosion, etc.

Aerated

Solution containing more than 10 ppb (parts per billion) oxygen.

Aeration

(1) Exposing to the action of air. (2) Causing air to bubble through. (3) Introducing air into a solution by spraying, stirring, or a similar method. (4) Supplying or infusing with air, as in sand or soil.

Aeration cell

An oxygen concentration cell; an electrolytic cell resulting from differences in dissolved oxygen at two points. See also differential aeration cell.

Age hardening

Hardening by aging, usually after rapid cooling or cold working.

Aging

A change in the properties of certain metals and alloys that occurs at ambient or moderately elevated temperatures after hot working or a heat treatment (quench aging in ferrous alloys, natural or artificial aging in ferrous and non-ferrous alloys) or after a cold working operation (strain aging). The change in properties is often, but not always, due to a phase change (precipitation), but never involves a change in chemical composition of the metal or alloy.

Alclad

Composite wrought product comprised of an aluminum alloy core having on one or both surfaces a metallurgically bonded aluminum or aluminum alloy coating that is anodic to the core and thus electrochemically protects the core against corrosion.

Alkali metal

A metal in group lA of the periodic table; namely, lithium, sodium, potassium, rubidium, cesium, or francium. They form strongly alkaline hydroxides, hence the name.

Alkaline

Having the properties of an alkali. (2) Having a pH greater than 7.

Alkaline cleaner

A material blended from alkali hydroxides and such alkaline salts as borates, carbonates, phosphates, or silicates. The cleaning action may be enhanced by the addition of surface-active agents and special solvents.

Alkyd

A resin used in coatings; reaction product of polyhydric alcohols and polybasic acids.

Alkylation

(1) A chemical process in which an alkyl radical is introduced into an organic compound by substitution or addition. (2) A refinery process for chemically combining isoparaffin with olefin hydrocarbons.

Alligatoring

(1) Pronounced wide cracking over the entire surface of a coating having the appearance of alligator hide. (2) The longitudinal splitting of flat slabs in a plane parallel to the rolled surface. Also called fish-mouthing.

Alloy plating

The code position of two or more metallic elements.

Alloy steel

One that contains either silicon or manganese in amounts in excess of those quoted in plain carbon steel or that contains any other element, or elements, as the result of deliberate alloying additions.

Alpha iron

The body-centered cubic form of pure iron, stable below 910 °C (l670 °F).

Alternate immersion test

A corrosion test in which the specimens are intermittently exposed to a liquid medium at definite time intervals.

Aluminizing

Process for impregnating the surface of a metal with aluminum in order to obtain protection from oxidation and corrosion.

Amalgam

An alloy of mercury with one or more other metals.

Ammeter

An instrument for measuring the magnitude of electric current flow.

Amorphous solid

A rigid material whose structure lacks crystalline periodicity; that is, the pattern of its constituent atoms or molecules does not repeat periodically in three dimensions. See also metallic glass.

Amphoteric

A term applied to oxides and hydroxides that can act as a base toward strong acids and as an acid toward strong alkalis; substances that can dissociate electrolytically to produce hydrogen or hydroxyl ions according to conditions.

Anaerobic

In the absence of air, or unreacted or free oxygen.

Anchor pattern/surface profile

Shape and amplitude of profile of blast cleaned or grooved steel that influences the bond between metallic or painted films and the substrate.

Anchorite

A zinc-iron phosphate coating for iron and steel.

Anion

Negatively charged ion, which migrates to the anode of a galvanic or voltaic cell.

Annealing

A generic term denoting a treatment, consisting of heating to and holding at a suitable temperature, followed by cooling at a suitable rate, used primarily to soften metallic materials, but also to simultaneously produce micro-structure. The purpose of such changes may be, but is not confined to, improvement of machinability, facilitation of cold work, improvement of mechanical or electrical properties, and/or increase in stability of dimensions. When the term is used by itself, full annealing is implied. When applied only for the relief of stress, the process is properly called stress relieving or stress-relief annealing.

Anode

An electrode at which oxidation of the surface or some component of the solution is occurring.

Anode corrosion

The dissolution of a metal acting as an anode.

Anode corrosion efficiency

Ratio of actual to theoretical corrosion based on the total current flow calculated by Faraday's law from the quantity of electricity that has passed.

Anode effect

The effect produced by polarization of the anode in electrolysis. It is characterized by a sudden increase in voltage and a corresponding decrease in amperage due to the anode becoming virtually separated from the electrolyte by a gas film.

Anode efficiency

Current efficiency of the anode

Anode film

(1) The portion of solution in immediate contact with the anode, especially if the concentration gradient is steep. (2) The outer layer of the anode itself.

Anode polarization

The difference between the potential of an anode passing current and equilibrium potential (or steady-state potential) of an electrode having the same electrode reaction.

Anodic cleaning

Electrolytic cleaning in which the work is at the anode. Also called reverse-current cleaning.

Anodic coating

A film on a metal surface resulting from an electrolytic treatment at the anode.

Anodic inhibitor

A chemical substance or combination of substances that prevent or reduce, by physical, physiochemical, or chemical action, the rate of the anodic or oxidation reaction.

Anodic metallic coating

A coating, composed wholly or partially of an anodic metal (in sufficient quantity to set off an electrochemical reaction) that is electrically positive to the substrate to which it is applied.

Anodic polarization

The change in the initial anode potential resulting from current flow effects at or near the anode surface. Potential becomes more noble (more positive) because of anodic polarization.

Anodic potential

An appreciable reduction in corrosion by making a metal into an anode, and maintaining this highly polarized condition with very little current flow.

Anodic protection

A technique to reduce corrosion of a metal surface under certain conditions, by passing sufficient anodic current through it to cause its electrode potential to enter and remain in the passive region.

Anodic reaction

Electrode reaction equivalent to a transfer of positive charge from the electronic to the ionic conductor. An anodic reaction is an oxidation process. An example common in corrosion is $Me \sim Me^{n+} + ne$.

Anodizing

Forming a conversion coating on a metal surface by anodic oxidation; most frequently applied to aluminum.

Anolyte

The electrolyte adjacent to the anode in an electrolytic cell.

Anti-fouling

Intended to prevent fouling of underwater structures, such as the bottoms of ships; refers to the prevention of attachment or growth of marine organisms on a submerged metal surface, generally through chemical toxicity caused by the composition of the metal or coating layer.

Anti-pitting agent

An addition agent for electroplating solutions to prevent the formation of pits or large pores in the electrodeposit.

Aqueous

Pertaining to water; an aqueous solution is a water solution.

Artificial aging

Aging above room temperature. See also aging. Compare with natural aging.

Atmospheric corrosion
The gradual degradation or alteration of a material by contact with substances present in the atmosphere, such as oxygen, carbon dioxide, water vapor, and sulfur, and chlorine compounds.

Austenite
A solid solution of one or more elements in face-centered cubic iron. Unless otherwise designated (such as nickel austenite) the solute is generally assumed to be carbon.

Austenitic
The name given to the face-centered cubic crystal structure (FCC) of ferrous metals. Ordinary iron and steel have this structure at elevated temperatures; also certain stainless steels (300 series) have this structure at room temperature.

Austenitic stainless steel
Steel containing sufficient amounts of nickel, nickel and chromium, or manganese to retain austenite at atmospheric temperature.

Austenitizing
Forming austenite by heating a ferrous alloy into the transformation range (partial austenitizing) or above the transformation range (complete austenitizing). When used without qualification, the term implies complete austenitizing.

Automatic welding
Welding in which the welding variables and the means of making the weld are controlled by machine.

Auxiliary anode
In electroplating, a supplementary anode positioned so as to raise the current density on a certain area of the cathode and thus obtain better distribution of plating.

Auxiliary electrode
The electrode of an electrochemical cell that is used to transfer current to or from a test electrode; commonly used in polarization studies. It is usually made of non-corroding material.

Backfill
Material placed in a drilled hole to fill space around anodes, vent pipe, and buried components of a cathodic protection system.

Bactericide
Chemicals that kill bacteria.

Bainite
A metastable aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures below the pearlite, but above the martensite start temperature.

Banded structure
A segregated structure consisting of alternating nearly parallel bands of different composition, typically aligned in the direction of primary hot working.

Bandwidth (ultrasonics)
Range of frequencies around a mean value that constitutes the nominal frequency.

Base
A chemical substance that yields hydroxide ions (OH^-) when dissolved in water. Compare with acid.

Base metal
(1) The metal present in the largest proportion in an alloy; brass, for example, is a copper-based alloy. (2) An active metal that readily oxidizes, or that dissolves to form ions. (3) The metal to be brazed, cut, soldered, or welded. (4) After welding, that part of the metal that was not melted.

Beach marks
Macroscopic progression marks on a fatigue fracture or stress-corrosion cracking surface that indicate successive positions of the advancing crack front. The classic appearance is of irregular elliptical or semi-elliptical rings, radiating outward from one or more origins. Beach marks (also known as clamshell marks or arrest marks) are typically found on service fractures where the part is loaded randomly, intermittently, or with periodic variations in mean stress or alternating stress. See also striation.

Bead
A single run of weld metal on a surface.

Bimetallic corrosion (galvanic corrosion)
Corrosion resulting from dissimilar metal contact.

Biocide
A chemical which kills other forms of life in addition to bacteria.

Biological corrosion
Biological corrosion is not a type of corrosion; it is the deterioration of a metal by corrosion processes that occur directly or indirectly as a result of the activity of living organisms. These organisms include micro forms such as bacteria and macro types such as algae and barnacles. Microscopic and macroscopic organisms have been observed to live and reproduce in media with pH values between 0 and 11, temperatures between −1.1 °C (30 °F) and 82.2 °C (180 °F), and under pressures up to 1020 bar (15 000 lb/in^2). Thus, biological activity may influence corrosion in a variety of environments, including soil, natural water, and seawater, natural petroleum products, and oil emulsion-cutting fluids.

Biostat
A chemical which retards the growth of other forms of life in addition to bacteria.

Bipolar electrode
An electrode in an electrolytic cell that is not mechanically connected to the power supply, but is so placed in the electrolyte, between the anode and cathode, such that the part nearer the anode becomes cathodic and the part nearer the cathode becomes anodic. Also called an intermediate electrode.

Bituminous coating
Coal tar or asphalt-based coating.

Black liquor
The liquid material remaining from pulpwood cooking in the soda or sulfate paper-making process.

Black oxide

A black finish on a metal produced by immersing it in hot oxidizing salts or salt solutions.

Blast cleaning

Cleaning and roughening of a surface (particularly steel) by the use of metallic grit or non-metallic grit or metal shot, which is projected against a surface by compressed air, centrifugal force, or water.

Blast peening

Treatment for relieving tensile stress by inducing beneficial compressive stress in the surface by the kinetic energy of rounded abrasive particles.

Blister

A raised area, often dome shaped, resulting from: (1) loss of adhesion between a coating or deposit and the base metal or (2) delamination under the pressure of expanding gas trapped in a metal in a near-sub-surface zone. Very small blisters may be called pinhead blisters or pepper blisters.

Blowdown

(1) Injection of air or water under high pressure through a tube into the anode area for the purpose of purging the annular space and possibly correcting high resistance caused by gas blocking. (2) In connection with boilers or cooling towers, the process of discharging a significant portion of the aqueous solution in order to remove accumulated salts, deposits, and other impurities.

Blue brittleness

Brittleness exhibited by some steels after being heated to a temperature within the range of about 200 to 370 °C (400 to 700 °F), particularly if the steel is worked at the elevated temperature.

Blushing

Whitening and loss of gloss of a usually organic coating caused by moisture. Also called blooming.

Bonderizing

A proprietary custom process for phosphatizing.

Brackish water

(1) Water having salinity values ranging from approximately 0.5 to l7 parts per thousand. (2) Water having less salt than seawater, but undrinkable.

Braze welding

The joining of metals using a technique similar to fusion welding, and a filler metal with a lower melting point than the parent metal, but neither using capillary action, as in brazing, nor intentionally melting the parent metal.

Brazing

A process of joining metals in which, during or after heating, molten filler metal is drawn by capillary action into the space between closed adjacent surfaces of the parts to be joined. In general, the melting point of the filler metal is above 500 °C, but always below the melting temperature of the parent metal.

Brazing alloy

Filler metal used in brazing.

Breakdown potential

The lowest noble potential where pitting or crevice corrosion, or both, will initiate and propagate.

Breakway corrosion
A sudden increase in corrosion rate, especially in high-temperature "dry" oxidation, etc.

Brightener
An agent or combination of agents added to an electroplating bath to produce a smooth, lustrous deposit.

Brine
Seawater containing a higher concentration of dissolved salt than that of the ordinary ocean.

Brittle fracture
Separation of a solid accompanied by little or no macroscopic plastic deformation. Typically, brittle fracture occurs by rapid crack propagation with less expenditure of energy than for ductile fracture.

Burning
(1) Permanently damaging a metal or alloy by heating to cause either incipient melting or intergranular oxidation. See also over-heating. (2) In grinding, getting the work hot enough to cause discoloration or to change the micro-structure by tempering or hardening.

Butt joint
A connection between the ends or edges of two parts making an angle to one another of 135° to 180° inclusive in the region of the joint.

Calcareous coating or deposit
A layer consisting of a mixture of calcium carbonate and magnesium hydroxide deposited on surfaces being cathodically protected because of the increased pH adjacent to the protected surface.

Calomel electrode
An electrode widely used as a reference electrode of known potential in electrometric measurement of acidity and alkalinity, corrosion studies, voltammetry, and measurement of the potentials of other electrodes.

Calorizing
Imparting resistance to oxidation to an iron or steel surface by heating in aluminum powder at 800 to 1000 °C (1470 to 1830 °F).

Carbon dioxide welding
Metal arc welding in which a bare wire electrode is used, the arc and molten pool being shielded with carbon dioxide gas.

Carbonitriding
A case-hardening process in which a suitable ferrous material is heated above the lower transformation temperature in a gaseous atmosphere of such composition as to cause simultaneous absorption of carbon and nitrogen by the surface and, by diffusion, create a concentration gradient. The process is completed by cooling at a rate that produces the desired properties in the work piece.

Carburization
The absorption of carbon into a metal surface; may or may not be desirable.

Carburizing
The absorption of carbon atoms by a metal at high temperatures; it may remain dissolved, or form metal carbides; absorption and diffusion of carbon into solid ferrous alloys by heating, to a temperature usually above Ac in contact with a suitable carbonaceous material. A form of case hardening that produces a carbon gradient extending inward from the surface, enabling the surface layer to be hardened either by quenching directly from the carburizing temperature or by cooling to room temperature then reaustenitizing and quenching.

Case hardening
A generic term covering several processes applicable to steel that change the chemical composition of the surface layer by absorption of carbon, nitrogen, or a mixture of the two, and, by diffusion, create a concentration gradient. The outer portion, or case, is made substantially harder than the inner portion, or core.

Cathode
The electrode of an electrolytic cell at which reduction occurs. In corrosion processes, usually the area at which metal ions do not enter the solution. Typical cathodic processes are cations taking up electrons and being discharged, oxygen being reduced, and reduction from a higher to a lower state of valency.

Cathode film
The portion of solution in immediate contact with the cathode during electrolysis.

Cathodic corrosion
Corrosion resulting from the cathodic condition of a structure, usually caused by the reaction of an amphoteric metal with the alkaline products of electrolysis.

Cathodic disbondment
The destruction of adhesion between a coating and its substrate by products of a cathodic reaction.

Cathodic inhibitor
A chemical substance or combination of substances that prevent or reduce the rate of cathodic reaction by a physical, physiochemical, or chemical action.

Cathodic pickling
Electrolytic pickling in which the work is at the cathode.

Cathodic polarization
Polarization of the cathode; a reduction from the initial potential resulting from current flow effects at or near the cathode surface. Potential becomes more active (negative) because of cathodic polarization.

Cathodic protection
(1) Reduction of corrosion rate by shifting the corrosion potential of the electrode toward a less oxidizing potential by applying an external electromotive force. (2) Partial or complete protection of a metal from corrosion by making it a cathode using either a galvanic or an impressed current. Contrast with anodic protection.

Cathodic reaction

Electrode reaction equivalent to a transfer of negative charge from the electronic to the ionic conductor. A cathodic reaction is a reduction process. An example common in corrosion is $Ox + ne \rightarrow Red$.

Catholyte

The electrolyte adjacent to the cathode of an electrolytic cell.

Cation

Positively charged ion that migrates to the cathode in a galvanic or voltaic cell.

Caustic

(1) Burning or corrosive. (2) A hydroxide of a light metal, such as sodium hydroxide or potassium hydroxide.

Caustic dip

A strongly alkaline solution into which metal is immersed for etching, for neutralizing acid, or for removing organic materials such as greases or paints.

Caustic embrittlement

An obsolete historical term denoting a form of stress-corrosion cracking most frequently encountered in carbon steels or iron-chromium-nickel alloys that are exposed to concentrated hydroxide solutions at temperatures of 200 to 250 °C (400 to 480 °F).

Cavitation (cavitation erosion)

Cavitation is a particular kind of erosion-corrosion caused by the formation and collapse of vapour bubbles in a liquid contacting a metal surface. The resultant shock forces reach high levels in local areas and can tear out jagged chunks of brittle materials or deform soft metals. Where the environment is corrosive, the severity of cavitation damage increases.

Cavitation damage

The degradation of a solid body resulting from its exposure to cavitation. This may include loss of material, surface deformation, or changes in properties or appearance.

Cell

A circuit consisting of an anode and a cathode in electrical contact in a solid or liquid electrolyte. Corrosion generally occurs only at anodic areas.

Cementation coating

A coating developed on a metal surface by a high-temperature diffusion process (as carburization, calorizing, or chromizing).

Cementite

A compound of iron and carbon, known chemically as iron carbide and having the approximate chemical formula Fe_3C. It is characterized by an orthorhombic crystal structure. When it occurs as a phase in steel, the chemical composition will be altered by the presence of manganese and other carbide-forming elements.

Chalking

The development of loose removable powder at the surface of an organic coating, usually caused by weathering.

Chamfering

The surface produced by bevelling an edge or corner.

Checking

The development of slight breaks in a coating that do not penetrate to the underlying surface.

Checks

Numerous, very fine cracks in a coating or at the surface of a metal part. Checks may appear during processing or during service and are most often associated with thermal treatment or thermal cycling. Also called check marks, checking, or heat checks.

Chelate

(1) A molecular structure in which a heterocyclic ring can he formed by the unshared electrons of neighboring atoms. (2) A co-cordination compound in which a heterocyclic ring is formed by a metal bound to two atoms of the associated ligand. See also complexation.

Chelating agent

(1) An organic compound in which atoms form more than one co-cordinate bond with metals in solution. (2) A substance used in metal finishing to control or eliminate certain metallic ions present in undesirable quantities.

Chelation

A chemical process involving formation of a heterocyclic ring compound that contains at least one metal cation or hydrogen ion in the ring.

Chemical cleaning

Method of surface preparation or cleaning involving the use of chemicals, with or without electrical force, for removal of mill scale, rust, sediments and paint. These chemicals can also be introduced into some systems on-stream while the system is operating.

Chemical conversion coating

A protective or decorative coating that is produced deliberately on a metal surface by reaction of the surface with a chosen chemical environment. The thin layer formed by this reaction may perform some or all of the following functions protect against corrosion; provide a base for organic coatings; improve retention of lubricants or compounds; improve abrasion resistance; provide an absorbent layer for rust-preventive oils and waxes.

Chemical potential

In a thermodynamic system of several constituents, the rate of change of the Gibbs function of the system with respect to the change in the number of moles of a particular constituent.

Chemical vapor deposition

A coating process, similar to gas carburizing and carbonitriding, whereby a reactant atmosphere gas is fed into a processing chamber where it decomposes at the surface of the work piece, liberating one material for either absorption by or accumulation on the work piece. A second material is liberated in gas form and is removed from the processing chamber, along with excess atmosphere gas.

Chemisorption

The binding of an adsorbate to the surface of a solid by forces whose energy levels approximate those of a chemical bond. Contrast with physisorption.

Chevron pattern

A fractographic pattern of radial marks (shear ledges) that look like nested letter "V"s; sometimes called a herringbone pattern. Chevron patterns are typically found on brittle fracture surfaces in parts whose widths are considerably greater than their thicknesses. The points of the chevrons can be traced back to the fracture origin.

Chromadizing

Improving paint adhesion on aluminum or aluminum alloys, mainly aircraft skins, by treatment with a solution of chromic acid. Also called chromodizing or chromatizing. Not to be confused with chromating or chromizing.

Chromate treatment

A treatment of metal in a solution of a hexavalent chromium compound to produce a conversion coating consisting of trivalent and hexavalent chromium compounds.

Chromating

Performing a chromate treatment.

Chrome pickle

(1) Producing a chromate conversion coating on magnesium for temporary protection or for a paint base. (2) The solution that produces the conversion coating.

Chromizing

A surface treatment at elevated temperature, generally carried out in pack, vapor, or salt bath, in which an alloy is formed by the inward diffusion of chromium into the base metal.

Clad metal

A composite metal containing two or more layers that have been bonded together. The bonding may have been accomplished by co-rolling, co-extrusion, welding, diffusion bonding, casting, heavy chemical deposition, or heavy electroplating.

Clad metals

Two metals rolled together so that the cheaper one forms a backing for the more costly one.

Cleavage

Splitting (fracture) of a crystal on a crystallographic plane of low index.

Cleavage fracture

A fracture, usually of polycrystalline metal, in which most of the grains have failed by cleavage, resulting in bright reflecting facets. It is associated with low-energy brittle fracture.

Co-ordination compound

A compound with a central atom or ion bound to a group of ions or molecules surrounding it. Also called co-ordination complex. See also chelate, complexation, and ligand.

Cold cracking

A type of weld cracking that usually occurs below 203 °C (400 °F). Cracking may occur during or after cooling to room temperature, sometimes with a considerable time delay. Three factors combine to produce cold cracks stress (for example, from thermal expansion and contraction), hydrogen (from hydrogen-containing welding consumables), and a susceptible micro-structure (plate martensite is most susceptible to cracking, ferritic and bainitic structures least susceptible). See also hot cracking, lamellar tearing, and stress-relief cracking.

Cold working

Deforming metal plastically under conditions of temperature and strain rate that induce strain hardening usually, but not necessarily, conducted at room temperature. Contrast with hot working.

Combined carbon

The part of the total carbon in steel or cast iron that is present as other than free carbon.

Compatibility

The ability of a given material to exist unchanged under certain conditions and environments in the presence of some other material.

Complexation

The formation of complex chemical species by the co-ordination of groups of atoms termed ligands to a central ion, commonly a metal ion. Generally, the ligand co-cordinates by providing a pair of electrons that forms an ionic or covalent bond to the central ion. See also chelate, co-cordination compound, and ligand.

Compressive

Pertaining to forces on a body or part of a body that tend to crush or compress the body.

Compressive strength

The maximum compressive stress a material is capable of developing. With a brittle material that fails in compression by fracturing, the compressive strength has a definite value. In the case of ductile, malleable, or semi-viscous materials (which do not fail in compression by a shattering fracture), the value obtained for compressive strength is an arbitrary value dependent on the degree of distortion that is regarded as effective failure of the material.

Compressive stress

A stress that causes an elastic body to deform (shorten) in the direction of the applied load. Contrast with tensile stress.

Concentration cell

An electrolytic cell, the emf of which is caused by a difference in concentration of some component in the electrolyte. (This difference leads to the formation of discrete cathode and anode regions).

Concentration polarization

That portion of the polarization of a cell produced by concentration changes resulting from passage of current through the electrolyte.

Conductivity

The ratio of the electric current density to the electric field in a material. Also called electrical conductivity or specific conductance.

Contact corrosion

A term primarily used in Europe to describe galvanic corrosion between dissimilar metals.

Contact plating

A metal plating process wherein the plating current is provided by galvanic action between the work metal and a second metal, without the use of an external source of current.

Contact potential

The potential difference at the junction of two dissimilar substances.

Continuity bond

A metallic connection that provides electrical continuity between metal structures.

Controlled galvanic system

Cathodic protection system using sacrificial anodes controlled by means of resistors, fixed or variable.

Conversion coating

A coating consisting of a compound of the surface metal, produced by chemical or electrochemical treatments of the metal. Examples include chromate coatings on zinc, cadmium, magnesium, and aluminum, and oxide and phosphate coatings on steel. See also chromate treatment and phosphating.

Copper ferrule

A ring or cap of copper put around a slender shaft (such as a cane or tool handle) to strengthen it or prevent splitting.

Copper-accelerated salt-spray (CASS) test

An accelerated corrosion test for some electrodeposits for anodic coatings on aluminum.

Corrodkote test

An accelerated corrosion test for electrodeposits.

Corrosion

The destruction of a substance, usually a metal, or its properties because of a reaction with its surroundings (environment) i.e. physiochemical interaction between a metal and its environment that results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system, of which these form a part.

Corrosion damage

A corrosion effect that is considered detrimental to the function of the metal, the environment or the technical system, of which these form a part.

Corrosion effect

A change in any part of the corrosion system caused by corrosion.

Corrosion embrittlement

The severe loss of ductility of a metal resulting from corrosive attack, usually intergranular and often not visually apparent.

Corrosion engineer

The person or persons responsible for carrying out the corrosion monitoring and interpretation of data produced.

Corrosion fatigue

The process in which a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment.

Corrosion fatigue limit

The maximum cyclic stress value that a metal can with withstand for a specified number of cycles or length of time in a given corrosive environment. See corrosion fatigue strength.

Corrosion fatigue strength

The maximum repeated stress that can be endured by a metal without failure under definite conditions of corrosion and fatigue, and for a specific number of stress cycles and a specified period of time.

Corrosion inhibitor

An inhibitor is a substance that retards or slows down a chemical reaction. Thus, a corrosion inhibitor is a substance that, when added to an environment, decreases the rate of attack by the environment on a metal. Corrosion inhibitors are commonly added in small amounts to acids, cooling water, oil wells, and other environments, either continuously or intermittently to prevent serious corrosion.

Corrosion potential

The potential of a corroding surface in an electrolyte, relative to a reference electrode.

Corrosion product

A substance formed as a result of corrosion.

Corrosion protection

Modification of a corrosion system so that corrosion damage is mitigated.

Corrosion rate

The rate at which corrosion proceeds, expressed by inches of penetration per year (ipy); mils penetration per year (mpy); milligrams weight loss per square decimeter per day (mdd); microns per year (μm/year), or millimeters per year (mmpy). One micron is equal to 0.0395 mils.

Corrosion resistance

Ability of a metal to withstand corrosion in a given corrosion system.

Corrosion system

System consisting of one or more metals and all parts of the environment that influence corrosion.

Corrosive agent

A substance that when in contact with a given metal will react with it.

Corrosive environment

An environment that contains one or more corrosive agents.

Corrosivity

Tendency of an environment to cause corrosion in a given corrosion system.

Couple

A cell developed in an electrolyte resulting from electrical contact between two dissimilar metals. See galvanic corrosion.

Coupons

Specimens of materials exposed to tests or real environments to assess the effect of degradation on the material.

Covered filler rod

A filler rod having a covering of flux.

Covering power

The ability of a solution to give satisfactory plating at very low current densities; a condition that exists in recesses and pits. This term suggests an ability to cover, but not necessarily to build up, a uniform coating, whereas throwing power suggests the ability to obtain a coating of uniform thickness of an irregularly shaped object.

Cracking

When a metal part fails by cracking, it is generally obvious that it cracked, but the exact type of cracking and the cause are less obvious. To determine the type of cracking, microscopic examination is necessary. In some instances the environment plays a minor role, while in others its role is major.

Cracking (of coating)

Breaks in a coating that extend through to the underlying surface.

Crazing

A network of checks or cracks appearing on the surface.

Creep

Time-dependent strain occurring under stress. The creep strain occurring at a diminishing rate is called primary creep, that occurring at a minimum and almost constant rate, secondary creep, and that occurring at an accelerating rate, tertiary creep.

Creep-rupture embrittlement

Embrittlement under creep conditions of, for example, aluminum alloys and steels that results in abnormally low rupture ductility. In aluminum alloys, iron in amounts above the solubility limit is known to cause such embrittlement; in steels, the phenomenon is related to the amount of impurities (for example, phosphorus, sulfur, copper, arsenic, antimony, and tin) present. In either case, failure occurs by intergranular cracking of the embrittled material.

Creep-rupture strength

The stress that will cause fracture in a creep test at a given time in a specified constant environment. Also called stress-rupture strength.

Crevice corrosion

Crevice corrosion is a special type of pitting. The anode of a corrosion cell is fixed by the geometry in a crevice or under a deposit. To function as a corrosion site, a crevice must be wide enough to permit entry of the liquid, but narrow enough to maintain a stagnant zone. Metals or alloys that depend on oxide films or passive layers for corrosion resistance are particularly susceptible to crevice corrosion.

Critical anodic current density

The maximum anodic current density observed in the active region for a metal or alloy electrode that exhibits active-passive behavior in an environment.

Critical flaw size

The size of a flaw (defect) in a structure that will cause failure at a particular stress level.

Critical humidity

The relative humidity (RH) at and above which the atmospheric corrosion rate of metal increases markedly.

Critical pitting potential (E_{cp}, E_p, E_{pp})

The lowest value of oxidizing potential at which pits nucleate and grow. It is dependent on the test method used.

CUI

Corrosion under insulation.

Current

The net transfer of electric charge per unit time. Also called electric current.

Current density

Denotes the average current flowing in the electrolyte expressed in amperes per square foot (A/ft^2), amperes per square decimeter (A/dm^2), amperes per square centimeter (A/cm^2) or milliamperes per square centimeter (mA/cm^2) of cathode or, more occasionally, of anode surface.

Current efficiency

The ratio of the electrochemical equivalent current density for a specific reaction to the total applied current density.

Deactivation

The process of prior removal of the active corrosive constituents, usually oxygen, from a corrosive liquid by controlled corrosion of expendable metal or by other chemical means, thereby making the liquid less corrosive.

De-alloying

The selective corrosion of one or more components of a solid solution alloy, usually in the form of ions. Also called parting or selective leaching.

Dealuminization

The selective leaching or corrosion of a specific constituent (Al, Ni, Mo, Ni) from an alloy.

Decarburization

Loss of carbon from the surface layer of a carbon-containing alloy due to reaction with one or more chemical substances in a medium that contacts the surface.

Decobaltification

Corrosion in which cobalt is selectively leached from cobalt-based alloys, such as Stellite, or from cemented carbides. See also dealloying and selective leaching.

Decomposition potential (or voltage)

The potential of a metal surface necessary to decompose the electrolyte of a cell or a component/substance thereof.

Deep ground bed

One or more anodes installed vertically at a nominal depth of 15 m (50 ft) or more below the earth's surface in a drilled hole for the purpose of supplying cathodic protection for an underground or submerged metallic structure. See also ground bed.

Demineralization

Removal of dissolved mineral matter, generally from water.

Dendrite

A crystal that has a tree-like branching pattern, being most evident in cast metals slowly cooled through the solidification range.

Denickelification

Corrosion in which nickel is selectively leached from nickel-containing alloys. Most commonly observed in copper-nickel alloys after extended service in fresh water.

Density (of gases)

The mass of a unit volume of a gas at a stated temperature and pressure.

Density (of solids and liquids)

The mass of unit volume of a material at a specified temperature.

Deoxidizing

(1) The removal of oxygen from molten metals by use of suitable deoxidizers. (2) Sometimes refers to the removal of undesirable elements other than oxygen by the introduction of elements or compounds that readily react with them. (3) In metal finishing, the removal of oxide films from metal surfaces by chemical or electrochemical reaction.

Depolarization

The elimination or reduction of polarization by physical or chemical means; depolarization results in increased corrosion.

Depolarizer

A substance that produces depolarization.

Deposit

A foreign substance that comes from the environment, adhering to a surface of a material.

Deposit attack

Pitting corrosion resulting from deposits on a metal surface that cause concentration cells.

Deposit corrosion

Corrosion occurring under or around a discontinuous deposit on a metallic surface. Also called poultice corrosion.

Deposited metal

Filler metal after it becomes part of a weld or joint.

Descaling

Removing the thick layer of oxides formed on some metals at elevated temperatures.

Dezincification

Corrosion in which zinc is selectively leached from zinc-containing alloys. Most commonly found in copper-zinc alloys containing less than 83% copper after extended service in water containing dissolved oxygen; the parting of zinc from an alloy (in some brasses, zinc is lost leaving a weak, brittle, porous, copper rich residue behind) See also dealloying and selective leaching.

Dichromate treatment

A chromate conversion coating produced on magnesium alloys in a boiling solution of sodium dichromate.

Dielectric shield

In a cathodic protection system, in electrically non-conductive material, such as a coating, plastic sheet or pipe, that is placed between an anode and an adjacent cathode to avoid current wastage and to improve current distribution, usually on the cathode.

Dielectric Strength

Degree of electrical non-conductance of a material; the maximum electric field a material can withstand without breakdown.

Differential aeration cell

An electrolytic cell, the electromotive force of which is due to a difference in air (oxygen) concentration at one electrode as compared with that at another electrode of the same material; an oxygen concentration cell (a cell resulting from a potential difference caused by different amounts of oxygen dissolved at two locations).

Diffusion Coating

Application of metallic coating, the chemical composition of which was modified by diffusing this at melting temperature into the substrate. Any process whereby a base metal or alloy is either (1) coated with another metal or alloy and heated to a sufficient temperature in a suitable environment or (2) exposed to a gaseous or liquid medium containing the other metal or alloy, thus causing diffusion of the coating or of the other metal or alloy into the base metal with resultant changes in the composition and properties of its surface.

Diffusion coefficient

A factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time.

Diffusion-limited current density

The current density, often referred to as limiting current density, that corresponds to the maximum transfer rate that a particular species can sustain because of the limitation of diffusion.

Dimple rupture

A fractographic term describing ductile fracture that occurs through the formation and coalescence of microvoids along the fracture path. The fracture surface of such a ductile fracture appears dimpled when observed at high magnification and usually is most clearly resolved when viewed in a scanning electron microscope.

Disbandment

The destruction of adhesion between a coating and the surface coated.

Discontinuity

Any interruption in the normal physical structure or configuration of a part, such as cracks, laps, seams, inclusions, or porosity. A discontinuity may or may not affect the usefulness of the part.

Dislocation

A linear imperfection in a crystalline array of atoms. Two basic types are recognized (1) an edge dislocation corresponds to the row of mismatched atoms along the edge formed by an extra, partial plane of atoms within the body of a crystal; (2) a screw dislocation corresponds to the axis of a spiral structure in a crystal, characterized by a distortion that joins normally parallel planes together to form a continuous helical ramp (with a pitch of one interplanar distance) winding about the dislocation.

Most prevalent is the so-called mixed dislocation, which is any combination of an edge dislocation and a screw dislocation.

DLA

Double layer activation.

Double layer

The interface between an electrode or a suspended particle and an electrolyte created by charge–charge interaction (charge separation) leading to an alignment of oppositely charged ions at the surface of the electrode or particle. The simplest model is represented by a parallel plate condenser of 2×10^{-8} cm in thickness. In general the electrode will be positively charged with respect to the solution.

Drainage

Conduction of electric current from an underground metallic structure by means of a metallic conductor. Forced drainage is that applied to underground metallic structures by means of an applied electromotive force or sacrificial anode. Natural drainage is that from an underground structure to a more negative (more anodic) structure, such as the negative bus of a trolley substation.

Dry corrosion

Gaseous corrosion.

Drying oil

An oil capable of conversion from a liquid to a solid by slow reaction with oxygen in the air.

Ductile fracture

Fracture characterized by tearing of metal accompanied by appreciable gross plastic deformation and expenditure of considerable energy. Contrast with brittle fracture.

Ductility

The ability of a material to deform plastically without fracturing, measured by elongation or reduction of area in a tensile test, by height of cupping in an Erichsen test, or by other means.

Dummy cathode

(1) A cathode, usually corrugated to give variable current densities, that is plated at low current densities to preferentially remove impurities from a plating solution. (2) A substitute cathode that is used during adjustment of operating conditions.

Dummying

Plating with dummy cathodes.

Dynamic equilibrium

The condition of an electrode when the rate of anodic dissolution just balances the rate of cathodic plating.

Edge preparation

Squaring, grooving, chamfering, or beveling an edge in preparation for welding.

Elastic deformation

A change in dimensions directly proportional to and in phase with an increase or decrease in applied force.

Elastic limit
The maximum stress that a material is capable of sustaining without any permanent strain (deformation) remaining upon complete release of the stress.

Elasticity
The property of a material by virtue of which deformation caused by stress disappears upon removal of the stress. A perfectly elastic body completely recovers its original shape and dimensions after release of stress.

Elastomer
A natural or synthetic polymer, which at room temperature can be stretched repeatedly to at least twice its original length, and which after removal of the tensile loud will immediately and forcibly return to approximately its original length.

Electrical conductivity
See conductivity.

Electrical isolation
The condition of being electrically separated from other metallic structures or the environment.

Electrical resistivity
The electrical resistance offered by a material to the flow of current, times the cross-sectional area of current flow and per unit length of current path; the reciprocal of the conductivity. Also called resistivity or specific resistance.

Electrochemical admittance
The inverse of electrochemical impedance.

Electrochemical cell
An electrochemical system consisting of an anode and a cathode in metallic contact and immersed in an electrolyte. (The anode and cathode may be different metals or dissimilar areas on the same metal surface.)

Electrochemical corrosion
Corrosion that is accompanied by a flow of electrons between cathodic and anodic areas on metallic surfaces.

Electrochemical equivalent
The weight of an element or group of elements oxidized or reduced at 100% efficiency by the passage of a unit quantity of electricity. Usually expressed as grams per coulomb (1 amp/s).

Electrochemical impedance
The frequency-dependent complex-valued proportionality factor (SE/6i) between the applied potential or current and the response signal. This factor is the total opposition of an electrochemical system to the passage of charge. The value is related to the corrosion rate under certain circumstances.

Electrochemical impedance spectroscopy (AC impedance)
A method to study the impedance of a metal/fluid interface by electrochemical properties by applying a sinusoidal polarization potential to the interface through a range of frequencies.

Electrochemical potential

The partial derivative of the total electrochemical free energy at a constituent with respect to the number of moles of this constituent where all factors are kept constant. It is analogous to the chemical potential of a constituent except that it includes the electric as well as chemical contributions to the free energy. The potential of an electrode in an electrolyte relative to a reference electrode measured under open circuit conditions.

Electrochemical series

Same as electromotive force series.

Electrode

(1) An electronic conductor used to establish electrical contact with an electrolytic part of a circuit. (2) An electronic conductor in contact with an ionic conductor.

Electrode polarization

Change of electrode potential with respect to a reference value. Often the free corrosion potential is used as the reference value. The change may be caused, for example, by the application of an external electrical current or by the addition of on oxidant or reductant.

Electrode potential

The potential of an electrode in an electrolyte, as measured against a reference electrode. The electrode potential does not include any resistance losses in potential in either the solution or the external circuit. It represents the reversible work to move a unit charge from the electrode surface through the solution to the reference electrode.The potential of an electrode as measured against a reference electrode. The electrode potential does not include any resistance loss in potential in solution due to the current passing to or from the electrode.

Electrode reaction

Interfacial reaction equivalent to a transfer of charge between electronic and ionic conductors. See also anodic reaction and cathodic reaction.

Electrode position

The deposition of a substance on an electrode by passing electric current through an electrolyte.

Electrogalvanising

Galvanized by electroplating.

Electrokinetic potential

This potential, sometimes called zeta potential, is a potential difference in the solution caused by residual, unbalanced charge distribution in the adjoining solution producing a double layer. The electrokinetic potential is different from the electrode potential in that it occurs exclusively in the solution phase; that is, it represents the reversible work necessary to bring a unit charge from infinity in the solution up to the interface in question, but not through the interface.

Electroless plating

A process in which metal ions in a dilute aqueous solution are plated out on a substrate by means of autocatalytic chemical reduction.

Electrolysis

Production of chemical changes of the electrolyte by the passage of current through an electrochemical cell.

Electrolyte
A chemical substance or mixture, usually liquid, containing ions that migrate in an electric field. (2) A chemical compound or mixture of compounds that when molten or in solution will conduct an electric current.

Electrolytic cell
An assembly, consisting of a vessel, electrodes, and an electrolyte, in which electrolysis can be carried out.

Electrolytic cleaning
A process of removing soil, scale, or corrosion products from a metal surface by subjecting it as an electrode to an electric current in an electrolytic bath; process of cleaning, degreasing, of a metal by making it an electrode in a suitable bath.

Electrolytic protection
Cathodic protection.

Electromotive force
Electrical potential; voltage.

Electromotive force series (emf series)
A list of elements arranged according to their standard electrode potentials (the hydrogen electrode is a reference point and given the value zero), with "noble" metals such as gold being positive and "active" metals such as zinc being negative.

Electron flow
A movement of electrons in an external circuit connecting an anode and cathode in a corrosion cell; the current flow is arbitrarily considered to be in an opposite direction to the electron flow.

Electron-beam welding
Fusion welding in which the joint is made by fusing the parent metal by the impact of a focused beam of electrons.

Electroplating
Electro deposition of a thin adherent layer of a metal or alloy of desirable chemical, physical and mechanical properties on metallic or non-metallic substrate.

Electropolishing
A technique commonly used to prepare metallographic specimens, in which a high polish is produced by making the specimen the anode in an electrolytic cell, where preferential dissolution at high points smooths the surface.

Electro-slag welding
A welding process in which consumable electrodes are fed into a joint containing flux; the current melts the flux, and the flux in turn melts the faces of the joint and the electrodes, allowing the weld metal to form a continuous cast ingot between the joint faces.

Electrotinning
Electroplating tin on an object.

Embrittlement

Severe loss of ductility of a metal (or alloy); loss of load carrying capacity of a metal or alloy; the severe loss of ductility or toughness or both, of a material, usually a metal or alloy. Many forms of embrittlement can lead to brittle fracture and many can occur during thermal treatment or elevated-temperature service (thermally induced embrittlement). Some of these forms of embrittlement, which affect steels, include blue brittleness, 885 °F (475 °C) embrittlement, quench-age embrittlement, sigma-phase embrittlement, strain-age embrittlement, temper embrittlement, tempered martensite embrittlement, and thermal embrittlement. In addition, steels and other metals and alloys can be embrittled by environmental conditions (environmentally assisted embrittlement). Forms of environmental embrittlement include acid embrittlement, caustic embrittlement, corrosion embrittlement, creep-rupture embrittlement, hydrogen embrittlement, liquid metal embrittlement, neutron embrittlement, solder embrittlement, solid metal embrittlement, and stress-corrosion cracking.

885 °F (475 °C) embrittlement

Embrittlement of stainless steels upon extended exposure to temperatures between 400 and 510 °C (730 and 930 °F). This type of embrittlement is caused by fine, chromium-rich precipitates that segregate at grain boundaries time at temperature directly influences the amount of segregation. Grain-boundary segregation of the chromium-rich precipitates increases strength and hardness, decreases ductility and toughness, and changes corrosion resistance. This type of embrittlement can be reversed by heating above the precipitation range.

Encapsulation

To protect the assembly by inhibited organic sealant, plastic caps, or cast potting compound.

Endurance limit

The maximum stress that a material can withstand for an infinitely large number of fatigue cycles; maximum cyclic stress level a metal can withstand without fatigue failure. See also fatigue strength.

Environment

The surroundings or conditions (physical, chemical, mechanical) in which a material exists.

Environmental cracking

Brittle fracture of a normally ductile material in which the corrosive effect of the environment is a causative factor. Environmental cracking is a general term that includes corrosion fatigue, high-temperature hydrogen attack, hydrogen blistering, hydrogen embrittlement, liquid metal embrittlement, solid metal embrittlement, stress-corrosion cracking, and sulfide stress cracking. The following terms have been used in the past in connection with environmental cracking, but are becoming obsolete caustic embrittlement, delayed fracture, season cracking, static fatigue, stepwise cracking, sulfide corrosion cracking, and sulfide stress-corrosion cracking. See also embrittlement.

Environmentally assisted embrittlement

See embrittlement.

Epoxy

Resin formed by the reaction of bisphenol and epichlorohydrin.

Equilibrium (reversible) potential

The potential of an electrode in an electrolytic solution when the forward rate of a given reaction is exactly equal to the reverse rate. The equilibrium potential can only be defined with respect to a specific electrochemical reaction.

Erosion

Destruction of metals by the abrasive action of moving fluids accelerated by the presence of solid particles in suspension. When corrosion occurs simultaneously, the term "erosion-corrosion" is often used.

Erosion and erosion-corrosion

Erosion is a strictly mechanical phenomenon, while erosion-corrosion is a combination of mechanical action and chemical or electrochemical reaction. Pure erosion seldom occurs in aqueous systems. Erosion-corrosion is characterized by grooves, gullies, waves, rounded holes and valleys, and usually exhibits a directional pattern. In copper alloy heat exchanger tubes, the attack frequently results in the formation of horseshoe-shaped depressions. Erosion-corrosion is the acceleration of metal loss because of the relative movement between a fluid and a metal surface. Generally, the movement is rapid, and the effects of mechanical wear are involved. Metal is removed as dissolved ions or as solid corrosion products that are swept from the surfaces.

Erosion-Corrosion

Corrosion which is increased because of the abrasive action of a moving stream; the presence of suspended particles greatly accelerates abrasive action.

Etch

To corrode the surface of a metal in order to reveal its composition and structure.

Eutectic

(1) An isothermal reversible reaction in which a liquid solution is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system. (2) An alloy having the composition indicated by the eutectic point on an equilibrium diagram. (3) An alloy structure of intermixed solid constituents formed by a eutectic reaction.

Eutectoid

(1) An isothermal reversible reaction in which a solid solution is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system. (2) An alloy having the composition indicated by the eutectoid point on an equilibrium diagram. (3) An alloy structure of intermixed solid constituents formed by a eutectoid reaction.

Exchange current

When an electrode reaches dynamic equilibrium in a solution, the rate of anodic dissolution balances the rate of cathodic plating. The rate at which either positive or negative charges enter or leav the surface at this point is known as the exchange current.

Exchange current density

The rate of charge transfer per unit area when an electrode reaches dynamic equilibrium (at its reversible potential) in a solution; that is, the rate of anodic charge transfer (oxidation) balances the rate of cathodic charge transfer (reduction).

Exfoliation

Exfoliation is a type of sub-surface corrosion that occurs and propagates as cracks approximately parallel to the surface. It leaves the metal in a laminated, flaky, or blistered condition, and appears most frequently in aluminum alloys or cupro-nickels.

External circuit

The wires, connectors, measuring devices, current sources, etc. that are used to bring about or measure the desired electrical conditions within the test cell. It is this portion of the cell through which electrons travel.

Failure

A general term used to imply that a part in service (1) has become completely inoperable, (2) is still, but is incapable of satisfactorily performing its intended function, or (3) has deteriorated seriously, to the point that it has become unreliable or unsafe for continued use.

Faraday's law

(1) The amount of any substance dissolved or deposited in electrolysis is proportional to the total electric charge passed. (2) The amounts of different substances dissolved or deposited by the passage of the same electric charge are proportional to their equivalent weights.

Fatigue

Subjecting a material to repeated stresses ultimately results in cracking. The environment may have an effect on the fatigue limit of a metal, though this is usually a minor factor. Generally, a fatigue failure is a single fracture, which is transgranular in most common metals. There is normally only a single fracture because stresses on other regions are relieved when the fracture occurs. Characteristic chevron patterns or beach marks can appear on the fracture face.

Fatigue crack growth rate

The rate of crack extension caused by constant-amplitude fatigue loading, expressed in terms of crack extension per cycle of load application.

Fatigue life

The number of cycles of stress that can be sustained prior to failure under a stated test condition.

Fatigue limit

The maximum stress that presumably leads to fatigue fracture in a specified number of stress cycles. If the stress is not completely reversed, the value of the mean stress, the minimum stress, or the stress ratio should also be stated. Compare with endurance limit.

Fatigue strength

The maximum stress that can be sustained for a specified number of cycles without failure, the stress being completely reversed within each cycle unless otherwise stated.

Ferrite

(1) A solid solution of one or more elements in body-centered cubic iron. Unless otherwise, designated (for instance as chromium ferrite), the solute is generally assumed to be carbon. On some equilibrium diagrams, there are two ferrite regions separated by an austenitic area. The lower area is α-ferrite; the upper δ-ferrite. If there is no designation, α-ferrite is assumed. (2) In the field of magnetism, substances having the general formula $M^{2+}O^{2-}$, $M_2{}^{3+}O_3{}^{2-}$, the trivalent metal often being iron.

Ferritic

Pertaining to the body-centered cubic crystal structure (BCC) of many ferrous (iron-based) metals.

Filiform corrosion

Corrosion that occurs under a film in the form of randomly distributed hairlines.

Filler metal
Metal added during welding, braze welding, brazing, or surfacing

Filler rod
Filler metal in the form of a rod. It may also take the form of filler wire.

Film
A thin, not necessarily visible, layer of material.

Fish eyes
Areas on a steel fracture surface having a characteristic white crystalline appearance.

Flakes
Short, discontinuous internal fissures in wrought metals attributed to stresses produced by localized transformation and decreased solubility of hydrogen during cooling after hot working. In a fracture surface, flakes appear as bright silvery areas; on an etched surface, they appear as short, discontinuous cracks. Also called shatter cracks or snowflakes.

Flame hardening
Hardening of metal surface by heating with oxyacetylene torch, followed by rapid cooling with water or air jet.

Flame spraying
Thermal spraying in which coating material is fed into an oxyfuel gas flame, where it is melted. Compressed gas may or may not be used to atomize the coating material and propel it onto the substrate.

Flux
Material used during welding, brazing, or braze welding to clean the surfaces of joint, prevent atmospheric, oxidation, and to reduce impurities.

Fogged metal
A metal whose luster has been reduced because of a surface film, usually a corrosion product layer.

Foreign structure
Any metallic structure that is not intended as part of a cathodic protection system of interest.

Fouling
An accumulation of deposits. This term includes accumulation and growth of marine organisms on a submerged metal surface and also includes the accumulation of deposits (usually inorganic) on heat exchanger tubing.

Fouling organism
Any aquatic organism with a sessile adult stage that attaches to and fouls underwater structures of ships.

Fractography
Descriptive treatment of fracture, especially in metals, with specific reference to photographs of the fracture surface. Macrofractography involves photographs at low magnification (<25×); microfractography, photographs at high magnification (>25×).

Fracture mechanics
A quantitative analysis for evaluating structural behavior in terms of applied stress, crack length, and specimen or machine component geometry.

Fracture toughness
A generic term for measures of resistance to extension of a crack. The term is sometimes restricted to results of fracture mechanics tests, which are directly applicable in fracture control. However, the term commonly includes results from simple tests of notched or precracked specimens not based on fracture mechanics analysis. Results from test of the latter type are often useful for fracture control, based on either service experience or empirical correlations with fracture mechanics tests.

Free carbon
The part of the total carbon in steel or cast iron that is present in elemental form as graphite or temper carbon. Contrast with combined carbon.

Free corrosion potential
Corrosion potential in the absence of net electrical current flowing to or from the metal surface.

Free ferrite
Ferrite that is formed directly from the decomposition of hypoeutectoid austenite during cooling, without the simultaneous formation of cementite. Also called proeutectoid ferrite.

Free machining
Pertains to the machining characteristics of an alloy to which one or more ingredients have been introduced to give small broken chips, lower power consumption, better surface finish, and longer tool life; among such additions are sulfur or lead to steel, lead to brass, lead and bismuth to aluminum, and sulfur or selenium to stainless steel.

Fretting
A type of wear that occurs between tight-fitting surfaces subjected to cyclic relative motion of extremely small amplitude. Usually, fretting is accompanied by corrosion, especially of the very fine wear debris. Fretting refers to metal deterioration caused by repetitive slip at the interface between two surfaces. When metal loss is increased by corrosion, the term “fretting corrosion” should be used.

Fretting corrosion
Another special case of erosion-corrosion, fretting corrosion, occurs when two heavily loaded metals rub rapidly together, causing damage to one or both metals. Vibration is usually responsible for the damage, but corrosion is also a factor because the frictional heat increases oxidation. In addition, mechanical removal of protective corrosion products continually exposes fresh metal. Fretting corrosion occurs more frequently in air than in water.

Furan
Resin formed from reactions involving furfuryl alcohol alone or in combination with other constituents.

Fusion penetration
Depth to which the parent metal has been fused.

Fusion welding
Welding in which the weld is made between metals in a molten state without the application of pressure.

Fusion zone
The part of the parent metal that is melted into the weld metal.

Galvanic
Pertaining to the current resulting from the coupling of dissimilar electrodes in an electrolyte.

Galvanic anode
A metal that because of its relative position in the galvanic series, provides sacrificial protection to metals that are more noble in the series, when coupled in an electrolyte.

Galvanic cell
A cell in that chemical change is the source of electrical energy. It usually consists of two dissimilar conductors in contact with each other and with an electrolyte, or of two similar conductors in contact with each other and with dissimilar electrolytes.

Galvanic corrosion
When two dissimilar metals are in contact with each other and exposed to a conductive environment, a potential exists between them, and a current flows. The less resistant metal becomes anodic, and the more resistant, cathodic. Attack on the less resistant metal increases, while on the more resistant one, it decreases.

Galvanic couple
A pair of dissimilar conductors, commonly metals, in electrical contact.

Galvanic couple potential
See mixed potential

Galvanic current
The electric current that flows between metals or conductive nonmetal in a galvanic couple.

Galvanic Series
A list of metals arranged according to their relative corrosion potentials in some specific environment; seawater is often used.

Galvanize
To coat a metal surface with zinc using any of various processes.

Galvanizing
The accepted term for the coating of iron or steel with zinc by the immersion of the metal in a bath of molten zinc. Galvanizing comes from “galvano”.

Galvanneal
To produce a zinc-iron alloy coating on iron or steel by keeping the coating molten after hot dip galvanizing until the zinc alloys completely with the base metal.

Galvanometer
An instrument for indicating or measuring a small electric current by means of a mechanical motion derived from electromagnetic or electrodynamic forces produced by the current.

Galvanostatic

An experimental technique where by an electrode is maintained at a constant current in an electrolyte.

Gamma iron

The face-centered cubic form of pure iron, stable from 910 to l400 °C (1670 to 2550 °F).

Gaseous corrosion

Corrosion with gas as the only corrosive agent and without any aqueous phase on the surface of the metal. Also called dry corrosion.

General corrosion

A form of deterioration that is distributed more or less uniformly over a surface; see also uniform corrosion.

Gibbs free energy

The thermodynamic function $\Delta G = \Delta H - T\Delta S$, where H is enthalpy, T is absolute temperature, and S is entropy. Also called free energy, free enthalpy, or Gibbs function.

Glass electrode

A glass membrane electrode used to measure pH or hydrogen-ion activity.

Grain

An individual crystal in a polycrystalline metal or alloy; it may or may not contain twinned regions and sub-grains; a portion of a solid metal (usually a fraction of an inch in size), in which the atoms are arranged in an orderly pattern.

Grain boundary

A narrow zone in a metal corresponding to the transition from one crystallographic orientation to another, thus separating one grain from another; the atoms in each grain are arranged in an orderly pattern; the irregular junction of two adjacent grains is known as a grain boundary.

Grain-boundary corrosion

Same as intergranular corrosion.

Graphitic corrosion

Deterioration of gray cast iron in which the metallic constituents are selectively leached or converted to corrosion products leaving the graphite intact. The term graphitization is commonly used to identify this form of corrosion, but is not recommended because of its use in metallurgy for the decomposition of carbide to graphite; deterioration of gray cast iron in which the metallic constituents are selectively leached or converted to corrosion products leaving the graphite intact.

Graphitization

A metallurgical term describing the formation of graphite in iron or steel, usually from decomposition of iron carbide at elevated temperatures. Not recommended as a term to describe graphitic corrosion.

Green liquor

The liquor resulting from dissolving molten melt iron form the recovery furnace in water.

Green rot

A form of high-temperature corrosion of chromium-bearing alloys in which green chromium oxide (Cr_2O_3) forms, but certain other alloy constituents remain metallic; some simultaneous carburization is sometimes observed.

Ground bed

A buried item, such as junk steel or graphite rods, that serves as the anode for the cathodic protection of pipelines or other buried structures.

Half cell

A pure metal in contact with a solution of known concentration of its own ion, at a specific temperature, develops a potential which is characteristic and reproducible; when coupled with another half cell, an overall potential develops that is the sum of both half cells.

Halogen

Any of the elements of the halogen family, consisting of fluorine, chlorine, bromine, iodine, and astatine.

Hard chromium

Chromium plated for engineering rather than decorative applications.

Hard water

Water that contains certain salts, such as those of calcium or magnesium, which form insoluble deposits in boilers and form precipitates with soap.

Hardenability

The relative ability of a ferrous alloy to form martensite when quenched from a temperature above the upper critical temperature. Hardenability is commonly measured as the distance below a quenched surface at which the metal exhibits a specific hardness (50 HRC, for example) or a specific percentage of martensite in the micro-structure.

Hardfacing

Depositing filler metal on a surface by welding, spraying, or braze welding to increase resistance to abrasion, erosion, wear, galling, impact, or cavitation damage.

Heat check

A pattern of parallel surface cracks that are formed by alternate rapid heating and cooling of the extreme surface metal, sometimes found on forging dies and piercing punches. There may be two sets of parallel cracks, one set perpendicular to the other.

Heat-affected zone (HAZ)

That portion of the base metal that was not melted during brazing, cutting, or welding, but whose micro-structure and mechanical properties were altered by the heat; refers to the area adjacent to a weld where the thermal cycle has caused micro-structural changes that generally affect corrosion behavior.

Hematite

(1) An iron mineral crystallizing in the rhombohedral system; the most important ore of iron. (2) An iron oxide, Fe_2O_3, corresponding to an iron content of approximately 70%.

Hermetic seal

An impervious seal made by the fusion of metals or ceramic materials (as by brazing, soldering, welding, fusing), which prevents the passage of gas or moisture.

High-temperature hydrogen attack

A loss of strength and ductility of steel by high-temperature reaction of absorbed hydrogen with carbides in the steel resulting in decarburization and internal fissuring.

Holidays

Discontinuities in a coating (such as porosity, cracks, etc.) that allow areas of base metal to be exposed to any corrosive environment that contacts the coated surface.

Hot corrosion

An accelerated corrosion of metal surfaces that results from the combined effect of oxidation and reactions with sulfur compounds and other contaminants, such us chlorides, to form a molten salt on a metal surface that fluxes, destroys, or disrupts the normal protective oxide. See also gaseous erosion.

Hot cracking

Also called solidification cracking, hot cracking of weldments is caused by the segregation at grain boundaries of low-melting constituents in the weld metal. This can result in grain-boundary tearing under thermal contraction stresses. Hot cracking can be minimized by the use of low-impurity welding materials and proper joint design. See also cold cracking, lamellar tearing, and stress-relief cracking.

Hot dip coating

A metallic coating obtained by dipping the base metal into a molten metal.

Hot shortness

A tendency for some alloys to separate along grain boundaries when stressed or deformed at temperatures near the melting point. Hot shortness is caused by a low-melting constituent, often present only in minute amounts, that is segregated at grain boundaries.

Hot working

Deforming metal plastically at such a temperature and strain rate that recrystallization takes place simultaneously with the deformation, thus avoiding any strain hardening. Contrast with cold working.

Huey test

Corrosion testing in a boiling solution of nitric acid. This test is mainly used to detect the susceptibility to intergranular corrosion of stainless steel.

Humidity test

A corrosion test involving exposure of specimens at controlled levels of humidity and temperature. Contrast with salt-fog test.

Hydrogen blistering

The formation of blisters on or below a metal surface from excessive internal hydrogen pressure; formation of blister-like bulges on a ductile metal surface caused by internal hydrogen pressures. Hydrogen may be formed during cleaning, plating, corrosion, and so forth.

Hydrogen damage

At moderate temperatures, hydrogen damage can occur as a result of a corrosion reaction on a surface or cathodic protection. Atomic hydrogen diffuses into the metal and collects at internal voids or laminations where it combines to form more voluminous molecular hydrogen. In steels, blisters sometimes occur. At higher temperatures and pressures, atomic hydrogen can diffuse into steel and collect at grain boundaries. Either molecular hydrogen is then formed, or the hydrogen reacts with iron carbides to form methane, resulting in cracking and decarburization. Hydrogen cracking is intergranular and highly branched, but not continuous.

Hydrogen disintegration

Deep internal cracks caused by hydrogen.

Hydrogen embrittlement

A process resulting in a decrease of the toughness or ductility of a metal due to the presence of atomic hydrogen. Hydrogen embrittlement has been recognized classically as being of two types. The first known as internal hydrogen embrittlement, occurs when the hydrogen enters molten metal that becomes supersaturated with hydrogen immediately after solidification. The second type, environmental hydrogen embrittlement, results from hydrogen being absorbed by solid metals. This can occur during elevated-temperature thermal treatments and in service during electroplating, contact with maintenance chemicals, corrosion reactions, cathodic protection, and operating in high-pressure hydrogen. In the absence of residual stress or external loading, environmental hydrogen embrittlement is manifested in various forms, such as blistering, internal cracking, hydride formation, and reduced ductility. With a tensile stress or stress-intensity factor exceeding a specific threshold, the atomic hydrogen interacts with the metal to induce sub-critical crack growth leading to fracture. In the absence of a corrosion reaction (polarized cathodically), the usual term used is hydrogen-assisted cracking (HAC) or hydrogen stress cracking (HSC). In the presence of active corrosion, usually as pits or crevices (polarized anodically), the cracking is generally called stress-corrosion cracking (SCC), but should more properly be called hydrogen-assisted stress-corrosion cracking (HSCC). Thus HSC and electrochemically anodic SCC can operate separately or in combination (HSCC). In some metals, such as high-strength steels, the mechanism is believed to be all, or nearly all, HSC. The participating mechanism of HSC is not always recognized and may be evaluated under the generic heading of SCC.

Hydrogen overvoltage

Overvoltage associated with the liberation of hydrogen gas.

Hydrogen probes

Probes designed to measure the permeation rate of atomic hydrogen H^+ (measured as hydrogen gas H_2) associated with hydrogen-induced cracking.

Hydrogen stress cracking (HSC)

Hydrogen embrittlement.

Hydrogen sulfide

Without H_2S: environment containing less than 1 ppm H_2S.
With H_2S: environment containing more than 1 ppm H_2S.
Low H_2S: greater than 3 ppm but less than 6 ppm H_2S.
High H_2S: More than 6 ppm H_2S.

Hydrogen-assisted cracking (HAC)

Hydrogen embrittlement.

Hydrogen-assisted stress-corrosion cracking (HSCC)

Hydrogen embrittlement.

Hydrogen-controlled electrode

A covered electrode that, when used correctly, produces less than a specified amount of diffusible hydrogen in the weld deposit.

Hydrogen-induced cracking (HIC)
Same as hydrogen embrittlement.

Hydrolysis
(1) Decomposition or alteration of a chemical substance by water. (2) In aqueous solutions of electrolytes, the reactions of cations with water to produce a weak base or of anions to produce a weak acid.

Hydrophilic
Having an affinity for water. Contrast with hydrophobic.

Hydrophobic
Lacking an affinity for, repelling, or failing to absorb or adsorb water. Contrast with hydrophilic.

Hygroscopic
(1) Possessing a marked ability to accelerate the condensation of water vapor; applied to condensation nuclei composed of salts that yield aqueous solutions of a very low equilibrium vapor pressure compared with that of pure water at the same temperature. (2) Pertaining to a substance whose physical characteristics are appreciably altered by effects of water vapor. (3) Pertaining to water absorbed by dry soil minerals from the atmosphere; the amounts depend on the physiochemical character of the surfaces, and increase with rising relative humidity.

Immersion plating
Depositing a metallic coating on a metal immersed in a liquid solution, without the aid of an external electric current. Also called dip plating.

Immunity
A state of resistance to corrosion or anodic dissolution of a metal caused by thermodynamic stability of the metal.

Impingement corrosion
A form of erosion-corrosion generally associated with the local impingement of a high-velocity, flowing fluid against a solid surface.

Impressed current
An electric current supplied by a power source that is external to the electrode system. (An example is DC current for cathodic protection.)

Impressed current protection
Cathodic protection of structures, where the cathodic polarization of metal is secured by electric currents emitted from an independent source.

Inclusions
Particles of foreign material in a metallic matrix. The particles are usually compounds (such as oxides, sulfides, or silicates), but may be of any substance that is foreign to (and essentially insoluble in) the matrix.

Incubation period
A period prior to the detection of corrosion while the metal is in contact with a corrodent.

Industrial atmosphere
An atmosphere in an area of heavy industry with soot, fly ash, and sulfur compounds as the principal constituents.

Inert anode
An anode that is insoluble in the electrolyte under the conditions prevailing in the electrolysis system.

Inhibitor
A chemical substance or combination of substances that, when present in the proper concentration and form in the environment, prevents or reduces corrosion.

Inorganic
Being or composed of matter other than hydrocarbons and their derivatives, or matter that is not of plant or animal origin. Contrast with organic.

Inorganic zinc-rich paint
Coating containing a zinc powder pigment in an inorganic vehicle.

Intensiostatic
Galvanostatic.

Intercrystalline corrosion
Intergranular corrosion.

Intercrystalline cracking
Intergranular cracking.

Interdendritic corrosion
Corrosive attack that progresses preferentially along interdendritic paths. This type of attack results from local differences in composition, such as coring commonly encountered in alloy castings.

Intergranular
Between crystals or grains. Also called intercrystalline. Contrast with transgranular.

Intergranular corrosion
Metals are composed of grains or crystals that form as solidification occurs. A crystal grows until it meets another advancing crystal. The regions of disarray between crystals are called grain boundaries, which differ in composition from the crystal center. Intergranular corrosion is the selective attack of the grain boundary or an adjacent zone. The most common example of intergranular corrosion is that of sensitized austenitic stainless steels in heat-affected zones at welds. Intergranular corrosion usually leaves the surface roughened, but definite diagnosis must be made by microscopic examination. Corrosion which occurs preferentially at grain boundaries.

Intergranular cracking
Cracking or fracturing that occurs between the grains or crystals in a polycrystalline aggregate. Also called intercrystalline cracking. Contrast with transgranular cracking.

Intergranular fracture
Brittle fracture of a metal in which the fracture is between the grains, or crystals, that form the metal. Also called intercrystalline fracture. Contrast with transgranular fracture.

Intergranular stress-corrosion cracking (IGSCC)
Stress-corrosion cracking in which the cracking occurs along grain boundaries.

Intermediate electrode
Same as bipolar electrode.

Internal oxidation
The formation of isolated particles of corrosion products beneath the metal surface. This occurs as the result of preferential oxidation of certain alloy constituents by inward diffusion of oxygen, nitrogen, sulfur, and so forth.

Intumescence
The swelling or bubbling of a coating usually because of heating (term currently used in space and fire protection applications).

Ion
An atom, or group of atoms, that has gained or lost one or more outer electrons and thus carries an electric charge. Positive ions, or cations, are deficient in outer electrons. Negative ions, or anions, have an excess of outer electrons.

Ion erosion
Deterioration of material caused by ion impact.

Ion exchange
The reversible interchange of ions between a liquid and solid, with no substantial structural changes in the solid.

Iron rot
Deterioration of wood in contact with iron-based alloys.

Isocorrosion diagram
A graph or chart that shows constant corrosion behavior with changing solution (environment) composition and temperature.

Killed steel
Thoroughly deoxidized steel, for example, by addition of aluminium or silicon, in which the reduction between carbon and oxygen during solidification is suppressed.

K_{ISCC}
Abbreviation for the critical value of the plane strain stress-intensity factor that will produce crack propagation by stress-corrosion cracking of a given material in a given environment.

Knifeline attack
Intergranular corrosion of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the sensitization temperature range.

Kraft process
Wood-pulping process in which sodium sulfate is used in the caustic soda pulp-digestion liquor. Also called kraft pulping or sulfate pulping.

Lamellar tearing

Occurs in the base metal adjacent to weldments due to high through-thickness strains introduced by weld metal shrinkage in highly restrained joints. Tearing occurs by decohesion and linking along the working direction of the base metal; cracks usually run roughly parallel to the fusion line and are step-like in appearance. Lamellar tearing can be minimized by designing joints to minimize weld shrinkage stresses and joint restraint. See also cold cracking, hot cracking, and stress-relief cracking.

Laminar scale

Rust formation in heavy layers.

Langelier saturation index

An index calculated from total dissolved solids, calcium concentration, total alkalinity, pH, and solution temperature that shows the tendency of a water solution to precipitate or dissolve calcium carbonate.

Ledeburite

The eutectic of the iron-carbon system, the constituents of which are austenite and cementite. The austenite decomposes into ferrite and cementite on cooling below the temperature at which transformation of austenite to ferrite or ferrite plus cementite is completed.

Ligand

The molecule, ion, or group bound to the central atom in a chelate or a co-cordination compound.

Limiting current density

The maximum current density that can be used to obtain a desired electrode reaction without undue interference, such as from polarization.

Linear elastic fracture mechanics

A method of fracture analysis that can determine the stress (or load) required to induce fracture instability in a structure containing a crack-like flaw of known size and shape. See also fracture mechanics and stress-intensity factor.

Linear polarization resistance (LPR)

At small applied polarization potentials, the relationship between applied potential approximates the polarization resistance. See also polarization resistance.

Lipophilic

Having an affinity for oil. See also hydrophilic and hydrophobic.

Liquid metal embrittlement

Catastrophic brittle failure of a normally ductile metal when in contact with a liquid metal and subsequently stressed in tension.

Local action

Corrosion due to the action of "local cells," that is, galvanic cells resulting from inhomogeneities between adjacent areas on a metal surface exposed to an electrolyte.

Local cell

A galvanic cell resulting from inhomogeneities between areas on a metal surface in an electrolyte. The inhomogeneities may be of a physical or a chemical nature in either the metal or its environment.

Localized corrosion

Corrosion at discrete sites, stress-corrosion cracking.

Long-line current

Current that flows through the earth from an anodic to a cathodic area of a continuous metallic structure. Usually used only where the areas are separated by considerable distance and where the current results from concentration-cell action.

Luggin probe (Luggin–Haber capillary)

A small tube or capillary filled with electrolyte, terminating close to the metal surface under study, and used to provide an ionically conducting path without diffusion between an electrode under study and a reference electrode.

Macroscopic

Visible at magnifications to 25×.

Macrostructure

The structure of metals as revealed by macroscopic examination of the etched surface of a polished specimen.

Magnetite

Naturally occurring magnetic oxide of iron (Fe_3O_4).

Manual welding

Welding in which the means of making the weld are held in the hand.

Martensite

A generic term for micro-structures formed by diffusionless phase transformation in which the parent and product phases have a specific crystallographic relationship. Martensite is characterized by an acicular pattern in the micro-structure in both ferrous and non-ferrous alloys. In alloys where the solute atoms occupy interstitial positions in the martensitic lattice (such as carbon in iron), the structure is hard and highly strained; but where the solute atoms occupy substitutional positions (such as nickel in iron), the martensite is soft and ductile. The amount of high-temperature phase that transforms to martensite on cooling depends to a large extent on the lowest temperature attained, there being a rather distinct beginning temperature (M_s) and a temperature at which the transformation is essentially complete (M_f).

Mechanical plating

Plating wherein fine metal powders are peened onto the work by tumbling or other means.

Metal arc welding

Arc welding using a consumable electrode.

Metal dusting

Accelerated deterioration of metals in carbonaceous gases at elevated temperatures to form a dust-like corrosion product; a unique form of high-temperature corrosion that forms a dust-like corrosion product and sometimes develops hemispherical pits on a susceptible metal surface; simultaneous carburization is generally observed.

Metal ion concentration cell

A galvanic cell caused by a difference in metal ion concentration at two locations on the same metal surface.

Metallic glass

An alloy having an amorphous or glassy structure. See also amorphous solid.

Metallizing

(1) The application of an electrically conductive metallic layer to the surface of nonconductors. (2) The application of metallic coatings by non-electrolytic procedures such as spraying of molten metal and deposition from the vapor phase.

Meteor perforation

Perforation of material in outer space resulting from meteor strikes.

Microbiologically-influenced corrosion (MIC)

Corrosion which is substantially increased as the result of the presence of bacteria (such as sulfate reducing bacteria, SRB or acid-producing bacteria, APB).

Microscopic

Visible at magnifications above 25×.

Microstructure

The structure of a prepared surface of a metal as revealed by a microscope at a magnification exceeding 25×.

MIG-welding

Metal inert gas arc welding using a consumable electrode.

Mill scale

An oxide layer on metals or alloys produced by metal rolling, hot forming, welding or heat treatment. Especially applicable to iron and steel.

Mixed potential

The potential of a specimen (or specimens in a galvanic couple) when two or more electrochemical reactions are occurring. Also called galvanic couple potential.

Molal solution

Concentration of a solution expressed in moles of solute divided by 1000 g of solvent.

Molar solution

Aqueous solution that contains 1 mole (gram-molecular weight) of solute in 1 L of the solution.

Mole

One mole is the mass numerically equal (in grams) to the relative molecular mass of a substance. It is the amount of substance of a system that contains as many elementary units (6.023×10^{23}) as there are atoms of carbon in 0.012 kg of the pure nuclide C12; the elementary unit must be specified and may be an atom, molecule, ion, electron, photon, or even a specified group of such units.

Monomer

A molecule usually an organic compound, having the ability to join with a number of identical molecules to form a polymer.

Noble metal

A metal that is not very reactive (such as silver, gold, or copper) and may be found naturally in metallic form on earth.

Normalizing

Heating a ferrous alloy to a suitable temperature above the transformation range and then cooling in air to a temperature substantially below the transformation range.

Open-circuit potential

The potential of an electrode measured with respect to a reference electrode or another electrode when no current flows to or from it.

Organic

Being or composed of hydrocarbons or their derivatives, or matter of plant or animal origin. Contrast with inorganic.

Organic acid

A chemical compound with one or more carboxyl groups (COOH) in its structure; examples are butyric acid, $CH_3(CH_2)_2COOH$; maleic acid, HOOCCH-CHCOOH; and benzoic acid, C_6H_5COOH.

Organic zinc coating

A paint containing zinc powder pigment and an organic (containing carbon) resin.

Organic zinc-rich paint

Coating containing zinc powder pigment and an organic resin.

Overaging

Aging under conditions of time and temperature greater than those required to obtain maximum change in a certain property, so that the property is altered in the direction of the initial value.

Overheating

Heating a metal or alloy to such a high temperature that its properties are impaired. When the original properties cannot be restored by further heat treating, by mechanical working, or by a combination of working and heat treating, the overheating is known as burning.

Overload

When a metal part has been subjected to a single stress beyond its tensile strength, it can fail by overload. The fracture can be either ductile or brittle, depending on factors such as the metal's hardness and operating temperature. In most cases, a single fracture results.

Overvoltage

The difference between the actual electrode potential when appreciable electrolysis begins and the reversible electrode potential.

Oxidation

(1) A reaction in which there is an increase in valence resulting from a loss of electrons. Contrast with reduction. (2) A corrosion reaction in which the corroded metal forms an oxide; usually applied to reaction with a gas containing elemental oxygen, such as air.

Oxidized surface (on steel)

Surface having a thin, tightly adhering, oxidized skin (from straw to blue in color), extending in from the edge of a coil or sheet.

Oxidizing agent

A compound that causes oxidation, thereby itself being reduced.

Oxyacetylene welding

Gas welding in which fuel gas is acetylene and which is burnt in an oxygen atmosphere.

Oxygen concentration cell

A galvanic cell resulting from difference in oxygen concentration between two locations. See also differential aeration cell.

Ozone

A powerfully oxidizing allotropic form of the element oxygen. The ozone molecule contains three atoms (O_3). Ozone gas is decidedly blue, and both liquid and solid ozone are an opaque blue-black color, similar to that of ink.

Parent metal

Metal to be joined, base metal.

Parkerizing

Trade name for process for the production of phosphate coating on steel articles by immersion in an aqueous solution of manganese or zinc acid with phosphate.

Partial annealing

An imprecise term used to denote a treatment given cold-worked material to reduce its strength to a controlled level or to effect stress relief. To be meaningful, the type of material, the degree of cold work, and the time-temperature schedule must be stated.

Parting

The selective attack of one or more components of a solid solution alloy; e.g. dezincification, dealumination etc. See also de-alloying.

Parts per billion (ppb)

A measure of proportion by weight, equivalent to one unit weight of a material per billion (10^9) unit weights of compound. One part per billion is equivalent to 1 mg/kg.

Parts per million (ppm)

A measure of proportion by weight, equivalent to one unit weight of a material per million (10^6) unit weights of compound. One part per million is equivalent to l mg/g.

Passivation

A reduction of the anodic reaction rate of an electrode involved in electrochemical action such as corrosion. Contrast with activation.

Passivator

A type of inhibitor that appreciably changes the potential of a metal to a more noble (positive) value.

Passive

The state of a metal when it is much more resistant to corrosion than its position in the emf series would predict. Passivation is a surface phenomenon.

Passive-active cell

(1) A cell, the emf of which is due to the potential difference between a metal in an active state and the same metal in a passive state. (2) A corrosion cell in which the anode is a metal in the active state and the cathode is the same metal in the passive state.

Passivity

A metal or alloy that is thermodynamically unstable in a given electrolytic solution is said to be passive when it remains visibly unchanged for a prolonged period. The following should be noted:

- During passivation the appearance may change if the passivating film is sufficiently thick (e.g. interference films).
- The electrode potential of a passive metal is always appreciably more noble than its potential in the active state.
- Passivity is an anodic phenomenon and thus control of corrosion by decreasing cathodic reactivity (e.g. amalgamated zinc in sulphuric acid) or by cathodic protection is not passivity.

Patina

The coating, usually green, that forms on the surface of metals such as copper and copper alloys exposed to the atmosphere. Also used to describe the appearance of a weathered surface of any metal.

Pearlite

A metastable lamellar aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures above the bainite range.

Peen plating

Deposition of the coating metal, in powder form, on the substrate by a tumbling action in presence of peening shot.

pH

A measure of the acidity or alkalinity of a solution; the negative logarithm of the hydrogen-ion activity; it denotes the degree of acidity or basicity of a solution. At 25 °C (77 °F), 7.0 is the neutral value. Decreasing values below 7.0 indicate increasing acidity; increasing values above 7.0, increasing basicity.

Phosphating

The forming of a thin inert phosphate coating on a surface, usually accomplished by treating with H_3PO_4 (phosphoric acid). Also called phosphatizing.

Phosphatizing

See phosphating.

Physical vapor deposition

A coating process whereby the cleaned and masked component to be coated is heated and rotated on a spindle above the streaming vapor generated by melting and evaporating a coating material source bar with a focused electron beam in an evacuated chamber.

Physisorption

The binding of an adsorbate to the surface of a solid by forces whose energy levels approximate those of condensation. Contrast with chemisorptions.

Pickle

A solution, usually acid, used to remove mill scale or other corrosion products from a metal.

Pickling

Form of chemical and electrolytic removal or loosening of mill scale and corrosion products from the surface of a metal in a chemical solution (usually acidic). Electrolytic pickling can be anodic or cathodic, depending on the polarization of the metal in the solution.

Pitting

Highly localized corrosion resulting in deep penetration at only a few spots.

Pitting factor

Ratio of the depth of the deepest pit resulting from corrosion divided by the average penetration, as calculated from weight loss.

Plane strain

The stress condition in linear elastic fracture mechanics in which there is zero strain in a direction normal to both the axis of applied tensile stress and the direction of crack growth (that is, parallel to the crack front); most nearly achieved in loading thick plates along a direction parallel to the plate surface. Under plane-strain conditions, the plane of fracture instability is normal to the axis of the principal tensile stress.

Plane stress

The stress condition in linear elastic fracture mechanics in which the stress in the thickness direction is zero; most nearly achieved in loading very thin sheet along a direction parallel to the surface of the sheet. Under plane-stress conditions, the plane of fracture instability is inclined 45° to the axis of the principal tensile stress.

Plasma plating

Deposition on critical areas of metal coatings resistant to wear and abrasion, by means of a high-velocity and high-temperature ionized inert gas jet.

Plasma spraying

A thermal spraying process in which the coating material is melted with heat from a plasma torch that generates a non-transferred arc molten coating material is propelled against the base metal by the hot, ionized gas issuing from the torch.

Plastic deformation

The permanent (inelastic) distortion of metals under applied stresses that strain the material beyond its elastic limit.

Plasticity

The property that enables a material to undergo permanent deformation without rupture.

Polarization

The deviation from the open circuit potential of an electrode resulting from the passage of current.

Polarization admittance

The reciprocal of polarization resistance (di/dE).

Polarization curve

A plot of r current density versus electrode potential for a specific electrode–electrolyte combination.

Polarization resistance

The slope (dE/di) at the corrosion potential of a potential (E) versus current density (i) curve. (It is inversely proportional to the corrosion current density when the polarization resistance technique is applicable).

Polyester

Resin formed by condensation of polybasic and monobasic acids with polyhydric alcohols.

Polymer

A chain of organic molecules produced by the joining of primary units called monomers.

Potential

Any of various functions from which intensity or velocity at any point in a field may be calculated. The driving influence of an electrochemical reaction. See also active potential, chemical potential, corrosion potential, critical pitting potential, decomposition potential, electrochemical potential, electrode potential, electrokinetic potential, equilibrium (reversible) potential, free corrosion potential, noble potential, open-circuit potential, protective potential, redox potential, and standard electrode potential.

Potential surveys

Measurement of potential of a structure or pipeline relative to a reference electrode potential pitting.

Potentiodynamic (potentiokinetic)

The technique for varying the potential of an electrode in a continuous manner at a preset rate.

Potentiostat

An electronic device that maintains an electrode at a constant potential; used in anodic protection devices.

Poultice corrosion

A term used in the automotive industry to describe the corrosion of vehicle body parts due to the collection of road salts and debris on ledges and in pockets that are kept moist by weather and washing. Also called deposit corrosion or attack.

Pourbaix (potential–pH) diagram

A plot of the redox potential of a corroding system versus the pH of the system, compiled using thermodynamic data and the Nernst equation. The diagram shows regions within which the metal itself or some of its compounds are stable.

Powder metallurgy

The art of producing metal powders and utilizing metal powders for production of massive materials and shaped objects.

Precious metal

One of the relatively scarce and valuable metals gold, silver, and the platinum-group metals. Also called noble metal(s).

Precipitation hardening

Hardening caused by the precipitation of a constituent from a supersaturated solution. See also age hardening and aging.

Precipitation heat treatment

Artificial aging in which a constituent precipitated from a supersaturated solid solution.

Precracked specimen

A specimen that is notched and subjected to alternating stresses until a crack has developed at the root of the notch.

Pressure welding

A welding process in which a weld is made by a sufficient pressure to cause plastic flow of the surfaces, which may or may not be heated.

Primary current distribution

The current distribution in an electrolytic cell that is free of polarization.

Primary passive potential (passivation potential)

The potential corresponding to the maximum active current density (critical anodic current density) of an electrode that exhibits active-passive corrosion behavior.

Primer

The first coat of paint applied to a surface. Formulated to have good bonding and wetting characteristics; may or may not contain inhibiting pigments.

Principal stress (normal)

The maximum or minimum value at the normal stress at a point in a plane considered with respect to all possible orientations of the considered plane. On such principal planes the shear stress is zero. There are three principal stresses on three mutually perpendicular planes. The state of stress at a point may be (1) uniaxial, a state of stress in which two of the three principal stresses are zero, (2) biaxial, a state of stress in which only one of the three principal stresses is zero, and (3) triaxial, a state of stress in which none of the principal stresses is zero. Multi-axial stress refers to either biaxial or triaxial stress.

Profile

Anchor pattern on a surface produced by abrasive blasting or acid treatment.

Protective potential

The threshold value of the corrosion potential that has to be reached to enter a protective potential range. The term used in cathodic protection to refer to the minimum potential required to suppress corrosion.

Protective potential range

A range of corrosion potential values in which acceptable corrosion resistance is achieved for a particular purpose.

Pulse width (ultrasonics)

Duration time of a single transmitted pulse.

Quench age embrittlement

Embrittlement of low-carbon steels resulting from precipitation of solute carbon of existing dislocations and from precipitation hardening of the steel caused by differences in the solid solubility of carbon in ferrite at different temperatures. Quench age embrittlement is usually caused by rapid cooling of the steel from a temperature slightly below AC1 (the temperature at which austenite begins to form), and can be minimized by quenching from lower temperatures.

Quench aging

Aging induced by rapid cooling after solution heat treatment.

Quench cracking

Fracture of a metal during quenching from elevated temperature. Most frequently observed in hardened carbon steel, alloy steel, or tool steel parts of high hardness and low toughness. Cracks often emanate from fillets, holes, corners, or other stress raisers, and result from high stresses due to the volume changes accompanying transformation to martensite.

Quench hardening

(1) In ferrous alloys, hardening by austenitizing and then cooling at a rate such that a substantial amount of austenite transforms to martensite. (2) In copper and titanium alloys hardening by solution treating and quenching to develop a martensite-like structure.

Quenching

Rapid cooling of metals (often steels) from a suitable elevated temperature. This generally is accomplished by immersion in water, oil, polymer solution, or salt, although forced air is sometimes used.

Radiation damage

A general term for the alteration of properties of a material arising from exposure to ionizing radiation (penetrating radiation), such as X-rays, gamma rays, neutrons, heavy-particle radiation, or fission fragments in nuclear fuel material.

Radiography (X-ray)

Use of X-rays to measure thickness or imperfections within solid materials.

Rare earth metal

One of the group of l5 chemically similar metals with atomic numbers 57 through 7l, commonly referred to as the lanthanides.

Reactive metal

A metal that readily combines with oxygen at elevated temperatures to form very stable oxides, for example, titanium, zirconium, and beryllium. Reactive metals may also become embrittled by the interstitial absorption of oxygen, hydrogen, and nitrogen.

Recrystallization

(1) Formation of a new, strain-free grain structure from that existing in cold worked metal, usually accomplished by heating. (2) The change from one crystal structure to another, as occurs on heating or cooling through a critical temperature.

Redox potential

The potential of a reversible oxidation-reduction electrode measured with respect to a reference electrode, corrected to the hydrogen electrode, in a given electrolyte.

Reducing agent

A compound that causes reduction, thereby itself becoming oxidized.

Reduction

A reaction in which there is a decrease in valence resulting from a gain in electrons. Contrast with oxidation.

Reference electrode

A non-polarizable electrode with a known and highly reproducible potential used for potentiometric and voltammetric analyses. See also calomel electrode.

Refractory metal

A metal having an extremely high melting point, for example, tungsten, molybdenum, tantalum, niobium, chromium, vanadium, and rhenium. In the broad sense, this term refers to metals having melting points above the range for iron, cobalt, and nickel.

Relative humidity

The ratio, expressed as a percentage, of the amount of water vapor present in a given volume of air at a given temperature to the amount required to saturate the air at that temperature.

Residual stress

Stresses that remain within a body as a result of plastic deformation.

Resistance

The opposition that a device or material offers to the flow of direct current, equal to the voltage drop across the element divided by the current through the element. Also called electrical resistance.

Resistance welding

Welding in which force is applied to surfaces in contact and in which the heat for welding is produced by the passage of electric current through the electrical resistance at, and adjacent to, these surfaces.

Resistivity

Electrical resistivity.

Resolution (ultrasonics)

The ability of a system to give simultaneous separate indications from discontinuities that are close together both in depth and lateral position

Rest potential

Corrosion potential and open-circuit potential.

Ringworm corrosion

Localized corrosion frequently observed in oil-well tubing in which a circumferential attack is observed near a region of metal "upset."

Riser

(1) That section of pipeline extending from the ocean floor up the platform. Also, the vertical tube in a steam generator convection bank that circulates water and steam upward. (2) A reservoir of molten metal connected to a casting to provide additional metal to the casting, required as the result of shrinkage before and during solidification.

Run

The metal method or deposited during one passage of an electrode, torch or blow-pipe.

Rust

A visible corrosion product consisting of hydrated oxides of iron. Applied only to ferrous alloys. See also white rust.

Rusting

Corrosion of iron or an iron-based alloy to form a reddish-brown product that is primarily hydrated ferric oxide.

Sacrificial anode

The use of an alloy electrode less noble than the structure to which it is connected, to induce galvanic corrosion on the electrode (anode) in preference to that of the structure.

Sacrificial protection/sacrificial anodes/sacrificial pieces

Pieces of metal which, being anodic to the equipment into which they are introduced, will galvanically corrode and so protect the equipment. Cathodic protection, based on wasting of anodic metal to prevent corrosion of cathodic metal – zinc, aluminum, magnesium, carbon steel, etc. – so protecting steel and other more noble metals.

Salt fog test

An accelerated corrosion test in which specimens are exposed to a fine mist of a solution usually containing sodium chloride, but sometimes modified with other chemicals.

Salt spray test

See salt fog test.

Saturated calomel electrode

A reference electrode composed of mercury, mercurous chloride (calomel), and a saturated aqueous chloride solution.

Scaling

(1) The formation at high temperatures of thick corrosion product layers on a metal surface. (2) The deposition of water-insoluble constituents on a metal surface.

Season cracking

An obsolete historical term usually applied to stress-corrosion cracking of brass.

Selective corrosion

The selective corrosion of certain alloying constituents from an alloy (as dezincification), or in an alloy (as internal oxidation).

Selective leaching

Selective leaching describes a corrosion process also called “parting” or de-alloying. More specifically, it can be called dezincification in the case of brasses, denickelification in cupro-nickels, etc. Selective leaching may occur in a plug form or in a more evenly distributed layer type. Stagnant conditions and regions under deposits are conductive to selective leaching. In brasses it can occur at pH extremes in water; high dissolved solids and high temperature also promote selective leaching. The overall dimensions of a part do not change drastically, but appreciable weakening can occur.

Semi-automatic welding

Welding in which some of the variables are automatically controlled, but manual guidance is necessary.

Sensitization

In austenitic stainless steels the precipitation of chromium carbide usually at grain boundaries, on exposure to temperatures of about 550 to 850 °C.

Sensitization heat treatment

A heat treatment, whether accidental, intentional, or incidental (as during welding) that causes precipitation of constituents at grain boundaries, often causing the alloy to become susceptible to intergranullar corrosion, cracking or stress corrosion cracking.

Shear

That type of force that causes or tends to cause two contiguous parts of the same body to slide relative to each other in a direction parallel to their plane of contact.

Shear strength

The stress required to produce fracture in the plane of cross section, the conditions of loading being such that the directions of force and of resistance are parallel and opposite although their paths are offset a specified minimum amount. The maximum load divided by the original cross-sectional area of a section separated by shear.

Sherodising

The coating of iron or steel with zinc by heating the product to be coated in zinc powder at a temperature below the melting point of zinc.

Sigma phase

A hard, brittle, non-magnetic intermediate phase with a tetragonal crystal structure, containing 30 atoms per unit cell, space group $P4_2mnm$, occurring in many binary and ternary alloys of the transition elements. The composition of this phase in the various systems is not the same and the phase usually exhibits a wide range in homogeneity. Alloying with a third transition element usually enlarges the field of homogeneity and extends it deep into the ternary section.

Sigma-phase embrittlement

Embrittlement of iron-chromium alloys (most notably austenitic stainless steels) caused by precipitation at grain boundaries of the hard, brittle intermetallic sigma phase during long periods of exposure to temperatures between approximately 560 and 980 °C (1050 and 1800 °F). Sigma-phase embrittlement results in severe loss of toughness and ductility, and can make the embrittled material susceptible to intergranular corrosion. See also sensitization.

Slip

Plastic deformation by the irreversible shear displacement (translation) of one part of a crystal relative to another in a definite crystallographic direction and usually on a specific crystallographic plane. Sometimes called glide.

Slow strain rate technique

An experimental technique for evaluating susceptibility to stress-corrosion cracking. It involves pulling the specimen to failure in uniaxial tension at a controlled slow strain rate while the specimen is in the test environment and examining the specimen for evidence of stress-corrosion cracking.

Slushing compound

An obsolete term describing oil or grease coatings used to provide temporary protection against atmospheric corrosion.

Smelt

Molten slag; in the pulp and paper industry, the cooking chemicals tapped from the recovery boiler as molten material and dissolved in the smelt tank as green liquor.

S–N diagram
A plot showing the relationship of stress, S, and the number of cycles, N, before fracture in fatigue testing.

Soft water
Water that is free of magnesium or calcium salts.

Soil resistivity
The electrical resistivity of the soil. This is important in cathodic protection systems as it affects current distribution through the soil and potentials on the protected structure.

Solder embrittlement
Reduction in mechanical properties of a metal as a result of local penetration of solder along grain boundaries.

Solid solution
A single, solid, homogeneous crystalline phase containing two or more chemical species. Solute; the component of either a liquid or solid solution that is present to a lesser or minor extent; the component that is dissolved in the solution.

Solid-metal embrittlement
The occurrence of embrittlement in a material below the melting point of the embrittling species. See also liquid-metal embrittlement.

Solution
In chemistry, a homogeneous dispersion of two or more kinds of molecular or ionic species. The solution may be composed of any combination of liquids, solids, or gases, but they always consist of a single phase.

Solution heat treatment
Heating an alloy to a suitable temperature, holding at that temperature long enough to cause one or more constituents to enter into solid solution, and then cooling rapidly enough to hold these constituents in solution.

Solution potential
Electrode potential where half-cell reaction involves only the metal electrode and its ion.

Solvent
The component of either a liquid or solid solution that is present to a greater or major extent; the component that dissolves the solute.

Sour gas
A gaseous environment containing hydrogen sulfide and carbon dioxide in hydrocarbon reservoirs. Prolonged exposure to sour gas can lead to hydrogen damage, sulfide-stress cracking, and/or stress-corrosion cracking in ferrous alloys.

Sour water
Waste waters containing fetid materials, usually sulfur compounds.

Spalling
The spontaneous chipping, fragmentation, or separation of a surface or surface coating.

Spatter

Globules of metal expelled during welding onto the surface of parent metal or of a weld.

Spelter

A brazing alloy consisting nominally of 50% Cu and 50% Zn.

Spheroidite

An aggregate of iron or alloy carbides of essentially spherical shape dispersed throughout a matrix of ferrite.

Sputtering

A coating process whereby thermally emitted electrons collide with inert gas atoms, which accelerate toward and impact a negatively charged electrode that is a target of the coating material. The impacting ions dislodge atoms of the target material, which are in turn projected to and deposited on the substrate to form the coating.

Stabilizing treatment

(1) Before finishing to final dimensions, repeatedly heating a ferrous or non-ferrous part to or slightly above its normal operating, temperature and then cooling to room temperature to ensure dimensional stability in service. (2) Transforming retained austenite in quenched hardenable steels, usually by cold treatment. (3) Heating a solution-treated stabilized grade of austenitic stainless steel to 870 to 900 °C (1600 to 1650 °F) to precipitate all carbon, as TiC, NbC, or TaC so that sensitization is avoided on subsequent exposure to elevated temperature.

Standard electrode potential

The reversible potential for an electrode process when all products and reactions are at unit activity on a scale in which the potential for the standard hydrogen half-cell is zero.

Steel:

- *Ferrite*
  The name given to the body-centered cubic allotropes of iron, and to body-centered cubic solid solutions
- *Austenite*
  The name given to the faced-centered cubic variety of iron, and to the face-centered cubic solid solutions.
- *Cementite*
  The name given to the carbide of iron, Fe_3C. This is an extremely hard and brittle constituent.
- Pearlite
  The eutectoid mixture of ferrite and cementite, formed when austenite decomposes during cooling. It consists of alternate thin layers, or lamellae, of ferrite and cementite.
- Martensite
  The name given to the very hard and brittle constituent that is formed when steel is very rapidly cooled from the austenitic state. It is a ferrite, highly supersaturated with dissolved carbon.
- Sorbite and troostite
  The names given to the structures produced when martensite or bainite is tempered, that is, heated to same temperature not exceeding 700 °C for the purpose of reducing brittleness and hardness.
- Bainite
  The term that is given to the decomposition product that is formed when austenite decomposes by either isothermal transformation, or at a cooling rate intermediate between the very rapid cooling necessary for martensite and the slower rate of cooling at which pearlite is formed.

- Plain carbon steel
  A steel containing up to 1.5% carbon together with not more than 0.5% silicon and not more than 1.5% manganese, and only traces of other elements.
- Alloy steel
  One that contains either silicon or manganese in amounts in excess of those quoted above, or that contains any other element, or elements, as the result of deliberately made alloying additions.

Strain

The unit of change in the size or shape of a body due to force. Also known as nominal strain.

Strain age embrittlement

A loss in ductility accompanied by an increase in hardness and strength that occurs when low-carbon steel (especially rimmed or capped steel) is aged following plastic deformation. The degree of embrittlement is a function of aging time and temperature, occurring in a matter of minutes at about 200 °C (400 °F), but requiring a few hours to a year at room temperature.

Strain aging

Aging induced by cold working.

Strain hardening

An increase in hardness and strength caused by plastic deformation at temperatures below the recrystallization range.

Strain rate

The time rate of straining for the usual tensile test. Strain as measured directly on the specimen gage length is used for determining strain rate. Because strain is dimensionless, the unit of strain rate is reciprocal time.

Stray current

Current flowing through paths other than the intended circuit.

Stray current corrosion

Stray current corrosion differs from other forms in that the source of the current causing the corrosion is external to the affected equipment. This cause of metal deterioration is frequently misdiagnosed. Stray-current corrosion can cause local metal loss in buried or submerged metal structures, but it occurs much less frequently in underwater transporting equipment than in underground structures. Stray-current corrosion is almost always associated with direct current. At the anodic areas, metal goes into solution and the electrolyte tends to become acidic. It is most commonly encountered in soils containing water.

Stress

The intensity of the internally distributed forces or components of forces that resist a change in the volume or shape of a material that is or has been subjected to external forces. Stress is expressed in force per unit area and is calculated on the basis of the original dimensions of the cross section of the specimen. Stress can be either direct (tension or compression) or shear. See also residual stress.

Stress concentration factor (K_t)

A multiplying factor for applied stress that allows for the presence of a structural discontinuity such as a notch or hole; K_t equals the ratio of the greatest stress in the region of the discontinuity to the nominal stress for the entire section. Also called theoretical stress concentration factor.

Stress corrosion cracking

Stress corrosion cracking is the result of the combined action of static stresses and corrosion. The static stresses may be residual or applied service stresses. The environment plays an important role in this type of cracking. The resulting cracks are branched, and can propagate either transgranularly or intergranularly, and sometimes both ways. Caustic cracking of steel is a case of stress corrosion cracking that is sometimes called caustic embrittlement. Generally speaking, it is not necessarily the concentration of the corrodent in the bulk environment that causes the cracking, but the increased concentration occurring in crevices or in alternately wetted and dried regions.

Stress corrosion or stress-accelerated corrosion

Corrosion which is accelerated by stress.

Stress intensity factor

A scaling factor, usually denoted by the symbol K, used in linear-elastic fracture mechanics to describe the intensification of applied stress at the tip of a crack of known size and shape. At the onset of rapid crack propagation in any structure containing, a crack, the factor is called the critical stress-intensity factor, or the fracture toughness. Various subscripts are used to denote different loading conditions or fracture toughnesses:

- K_c: Plane-stress fracture toughness. The value of stress intensity at which crack propagation becomes rapid in sections thinner than those in which plane-strain conditions prevail.
- K_I: Stress-intensity factor for a loading condition that displaced the crack faces in a direction normal to the crack plane (also known as the opening mode of deformation).K_{Ic}: Plane-strain fracture toughness. The minimum value of K_c for any given material and condition, which is attained when rapid crack propagation in the opening mode is governed by plane-strain conditions.
- Kid: Dynamic fracture toughness. The fracture toughness determined under dynamic loading conditions; it is used as an approximation of K_{Ic} for very tough materials.
- K_{ISCC}: Threshold stress-intensity factor for stress-corrosion cracking. The critical plane-strain stress intensity at the onset of stress-corrosion cracking under specified conditions.
- K_Q: Provisional value for plane-strain fracture toughness.
- K_{th}: Threshold stress intensity for stress-corrosion cracking. The critical stress intensity at the onset of stress-corrosion cracking under specified conditions.
- DK: The range of the stress-intensity factor during a fatigue cycle.

Stress raisers

Changes in contour or discontinuities in structure that cause local increases in stress.

Stress ratio, A or R

The algebraic ratio of two specified stress values in a stress cycle. Two commonly used stress ratios are (1) the ratio of the alternating stress amplitude to the mean stress. $A = S_a/S_m$ and (2) the ratio of the minimum stress to the maximum stress. $R = S_{min}/S_{max}$.

Stress-intensity factor range, DK

In fatigue, the variation in the stress-intensity factor in cycle, that is, $K_{max} - K_{min}$.

Stress-relief cracking

Also called postweld heat-treatment cracking, stress-relief cracking occurs when susceptible alloys are subjected to thermal stress relief after welding to reduce residual stresses and improve toughness. Stress-relief cracking occurs only in metals that can precipitation-harden during such elevated-temperature exposure; it usually occurs at stress raisers, is intergranular in nature, and is generally

observed in the coarse-grained region of the weld heat-affected zone. See also cold cracking, hot cracking, and lamellar tearing.

Striation

A fatigue fracture feature, often observed in electron micrographs, that indicates the position of the crack front after each succeeding cycle of stress. The distance between striations indicates the advance of the crack front across that crystal during one stress cycle, and a line normal to the striation indicates the direction of local crack propagation. See also beach marks.

Submerged arc welding

Metal-arc welding in which a bare wire electrode is used; the arc is enveloped in flux; some of which fuses to form a removable covering of slag on the weld.

Substrate

The basic metal or non-metal whose surface is being protected.

Subsurface corrosion

Formation of isolated particles of corrosion products beneath a metal surface. This results from the preferential reactions of certain alloy constituents to inward diffusion of oxygen, nitrogen, or sulfur.

Sulfidation

The reaction of a metal or alloy with a sulfur-containing species to produce a sulfur compound that forms on or beneath the surface on the metal or alloy.

Sulfide stress cracking

Brittle failure by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. See also environmental cracking.

Surface treatment

Any suitable means of cleaning and treating a surface that will result in the desired surface profile and cleanliness and the required coating characteristics.

Surfactant

A surface-active agent; usually an organic compound whose molecules contain a hydrophilic group at one end and a lipophilic group at the other.

Tafel line, Tafel slope, Tafel diagram

An electrode when polarized frequently yields a current potential relationship over a region which can be approximated by:

$$\mathrm{h} = \pm \mathrm{B} \log(i/i_0)$$

where h = change in open circuit potential, i = the current density, B and i_o = constants. B is known as the Tafel slope. If this behavior is observed a plot of the semi-logarithmic components is known as the Tafel line and the diagram is called the Tafel diagram.

Tarnish

Surface discoloration of a metal caused by formation of a thin film of corrosion product.

Temper

(1) In heat treatment, to reheat hardened steel or hardened cast iron to some temperature below the eutectoid temperature for the purpose of decreasing hardness and increasing toughness. The process is also sometimes applied to normalized steel. (2) In tool steels, temper is sometimes inadvisably used

to denote carbon content. (3) In non-ferrous alloys and in some ferrous alloys (steels that cannot be hardened by heat treatment), the hardness and strength produced by mechanical or thermal treatment, or both, and characterized by a certain structure, mechanical properties, or reduction of area during cold working.

Temper color

A thin, tightly adhering oxide skin (only a few molecules thick) that forms when steel is tempered at a low temperature, or for a short time, in air or a mildly oxidizing atmosphere. The color, which ranges from straw to blue depending on the thickness of the oxide skin, varies with both tempering time and temperature.

Temper embrittlement

Embrittlement of alloy steels caused by holding within or cooling slowly through a temperature range just below the transformation range. Embrittlement is the result of the segregation at grain boundaries of impurities such as arsenic, antimony, phosphorus, and tin; it is usually manifested as an upward shift in ductile-to-brittle transition temperature. Temper embrittlement can be reversed by retempering above the critical temperature range, then cooling rapidly.

Tempered martensite embrittlement

Embrittlement of ultra-high-strength steels caused by tempering in the temperature range of 205 to 400 °C (400 to 750 °F); also called 350 °C or 500 °F embrittlement. Tempered martensite embrittlement is thought to result from the combined effects of cementite precipitation on prior-austenite grain boundaries or interlath boundaries and the segregation of impurities at prior-austenite grain boundaries.

Tempering

To reheat hardened steel or hardened cast iron to some temperature below the eutectoid temperature for the purpose of decreasing hardness and increasing toughness.

Tensile strength

In tensile testing, the ratio of maximum load to original cross-sectional area. Also called ultimate tensile strength.

Tensile stress

A stress that causes two parts of an elastic body, on either side of a typical stress plane, to pull apart. Contrast with compressive stress.

Tension

The force or load that produces elongation.

Terne

An alloy of lead containing 3 to l5% Sn, used as a hot dip coating for steel sheet or plate. Terne coatings, which are smooth and dull in appearance, give the steel better corrosion resistance and enhance its ability to be formed, soldered, or painted.

Terne Plate

Deposition of lead-tin alloy on iron or steel sheets by the hot dip process.

Thermal cutting

The parting or shaping of materials by the application of heat with or without a stream of cutting oxygen.

Thermal electromotive force

The electromotive force generated in a circuit containing two dissimilar metals when one junction is at a temperature different from that of the other. See also thermocouple.

Thermal embrittlement

Intergranular fracture of maraging steels with decreased toughness resulting from improper processing after hot working. Thermal embrittlement occurs upon heating above l095 °C (2000 °F) and then slow cooling through the temperature range of 815 to 980 °C (1300 to l800 °F), and has been attributed to precipitation of titanium carbides and titanium carbonitrides at austenite grain boundaries during cooling through the critical temperature range.

Thermal spraying

A group of coating or welding processes in which finely divided metallic or non-metallic materials are deposited in a molten or semi-molten condition to form a coating. The coating material may be in the form of powder, ceramic rod, wire, or molten materials. See also flame spraying and plasma spraying.

Thermocouple

A device for measuring temperatures, consisting of lengths of two dissimilar metals or alloys that are electrically joined at one end and connected to a voltage-measuring instrument at the other end. When one junction is hotter than the other, a thermal electromotive force is produced that is roughly proportional to the difference in temperature between the hot and cold junctions.

Thermogalvanic corrosion

Corrosion resulting from an electrochemical cell caused by a thermal gradient.

Threshold stress

The critical gross section stress at the onset of stress-corrosion cracking under specified conditions.

Throwing power

(1) The relationship between the current density at a point on a surface and its distance from the counter electrode. The greater the ratio of the surface resistivity shown by the electrode reaction to the volume resistivity of the electrolyte, the better is the throwing power of the process. (2) The ability of a plating solution to produce a uniform metal distribution on an irregularly shaped cathode.

TIG-welding

Tungsten inert gas arc welding using a non-consumable electrode of pure or activated tungsten.

Tinning

Coating metal with a very thin layer of molten solder or brazing filler metal.

Torsion

A twisting deformation of a solid body about an axis in which lines that were initially parallel to the axis become helices.

Torsional stress

The shear stress on a transverse cross section resulting from a twisting action.

Total carbon

The sum of the free carbon and combined carbon (including carbon in solution) in a ferrous alloy.

Toughness
The ability of a metal to absorb energy and deform plastically before fracturing.

Transcrystalline
See transgranular.

Transcrystalline cracking
See transgranular cracking.

Transference
The movement of ions through the electrolyte associated with the passage of the electric current. Also called transport or migration.

Transgranular
Through or across crystals or grains. Also called intracrystalline or transcrystalline.

Transgranular cracking
Cracking or fracturing that occurs through or across a crystal or grain. Also called transcrystalline cracking. Contrast with intergranular cracking.

Transgranular fracture
Fracture through or across the crystals or grains of a metal. Also called ranscrystalline fracture or intracrystalline fracture. Contrast with intergranular fracture.

Transition metal
A metal in which the available electron energy levels are occupied in such away that the d-band contains less than its maximum number of 10 electrons per atom, for example, iron, cobalt, nickel, and tungsten. The distinctive properties of the transition metals result from the incompletely filled d-levels.

Transition temperature
(1) An arbitrarily defined temperature that lies within the temperature range in which metal fracture characteristics (as usually determined by tests of notched specimens) change rapidly, such as from primarily fibrous (shear) to primarily crystalline (cleavage) fracture. (2) Sometimes used to denote an arbitrarily defined temperature within a range in which the ductility changes rapidly with temperature.

Transpassive region
The region of an anodic polarization curve, noble to and above the passive potential range, in which there is a significant increase in current density (increased metal dissolution) as the potential becomes more positive (noble).

Transpassive state
(1) State of anodically passivated metal characterized by a considerable increase of the corrosion current, in the absence of pitting, when the potential is increased. (2) The noble region of potential where an electrode exhibits at higher than passive current density.

Triaxial stress
See principal stress (normal).

Tuberculation

The formation of localized corrosion products scattered over the surface in the form of knob-like mounds called tubercles.

U-bend specimen

Horseshoe-shaped test piece used to detect the susceptibility of a material to stress corrosion cracking.

Ultimate strength

The maximum stress (tensile, compressive, or shear) a material can sustain without fracture, determined by dividing maximum load by the original cross-sectional area of the specimen. Also called nominal strength or maximum strength.

Ultrasonic measurement

The timing of the transmission of ultrasonic sound waves through a material to determine the material's thickness.

Underfilm corrosion

Corrosion that occurs under organic films in the form of randomly distributed thread-like filaments or spots. In many cases this is identical to filiform corrosion.

Uniaxial stress

See principal stress (normal).

Uniform corrosion

(1) A type of corrosion attack (deterioration) uniformly distributed over metal surface. (2) Corrosion that proceeds at approximately the same rate over a metal surface. Also called general corrosion. General corrosion is characterized by a chemical or electrochemical reaction that occurs uniformly over the exposed surface. Anodic and cathodic sites shift constantly so that corrosion spreads over the entire metal surface. Identifying general corrosion is usually simple, but determining its cause is often difficult. Chemical dissolution by acids, bases or chelants frequently results in general corrosion.

Vacuum deposition/vapor depositions/gas plating

Deposition of metal coatings by the precipitation, sometimes in vacuum, of metal vapor on the treated surface. Vapor may be produced by thermal decomposition, cathode sputtering, or by evaporation of the molten metal in air or inert gas.

Valence

A positive number that characterizes the combining power of an element for other elements, as measured by the number of bonds to other atoms that one atom of the given element forms upon chemical combination hydrogen is assigned valence 1, and the valence is the number of hydrogen atoms, or their equivalent, with which an atom of the given element combines.

Vapor deposition

See chemical vapor deposition, physical vapor deposition and sputtering.

Vapor plating

Deposition of a metal or compound on a heated surface by reduction or decomposition of a volatile compound at a temperature below the melting points of the deposit and the base material. The reduction is usually accomplished by a gaseous reducing agent such as hydrogen. The decomposition process may involve thermal dissociation or reaction with the base material. Occasionally used to designate deposition on cold surfaces by vacuum evaporation. See also vacuum deposition.

Voids
A term generally applied to paints to describe holidays, holes, and skips in a film. Also used to describe shrinkage in castings and weld.

Vulcanizing
Treatment of rubber with sulfur or sulfur compounds resulting in a change in the physical properties of the rubber.

Wash primer
A thin, inhibiting paint, usually chromate pigmented with a polyvinyl butyrate binder.

Weather resistance
Ability of a material to resist all ambient weather conditions. These include changes of temperature, precipitation, effect of wind and humidity, sunlight, oxygen, and other gases, and impurities in the atmosphere, ultraviolet rays, radiation, and ozone.

Weld
A union between pieces of metal at faces rendered plastic or liquid by heat or by pressure, or by both. A filler metal whose melting temperature is of the same order as that of the parent metal may or may not be used.

Weld cracking
Cracking that occurs in the weld metal. See also cold cracking, hot cracking, lamellar tearing, and stress-relief cracking.

Weld decay
Intergranular corrosion, usually of stainless steels or certain nickel-base alloys, that occurs as the result of sensitization in the heat-affected zone during the welding operation.

Weld metal
All metal melted during the making of a weld and retained in the weld.

Weld zone
The zone containing the weld metal and the heat-affected zone.

Welding
The making of a weld.

Wetting
A condition in which the interfacial tension between a liquid and a solid is such that the contact angle is 0 to 90°.

Wetting agent
A substance that reduces the surface tension of a liquid, thereby causing it to spread more readily on a solid surface.

White liquor
Cooking liquor from the kraft pulping process produced by recausticizing green liquor with lime.

White rust
Zinc oxide the powdery product of corrosion of zinc or zinc-coated surfaces.

Work hardening

Same as strain hardening.

Working electrode

The test or specimen electrode in an electrochemical cell.

Yield

Evidence of plastic deformation in structural materials. Also called plastic flow or creep. See also flow.

Yield point

The first stress in a material, usually less than the maximum attainable stress, at which an increase in strain occurs without an increase in stress. Only certain metals – those that exhibit a localized, heterogeneous type of transition from elastic deformation to plastic deformation – produce a yield point. If there is a decrease in stress after yielding, a distinction may be made between upper and lower yield points. The load at which a sudden drop in the flow curve occurs is called the upper yield point. The constant load shown on the flow curve is the lower yield point.

Yield strength

The stress at which a material exhibits a specified deviation from proportionality of stress and strain. An onset of 0.2% is used for many metals.

Yield stress

The stress level in a material at or above the *yield* strength but below the ultimate strength, i.e. a stress in the plastic range.

Zeta potential

Electrokinetic potential.

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