

# 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.

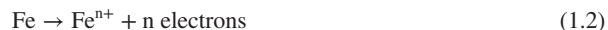
Oil and gas production operations consume a tremendous amount of iron and steel pipe, tubing, pumps, valves, and sucker rods. Leaks cause loss of oil and gas, and also permit infiltration of water and silt, thus increasing corrosion damage. Saline water and sulfides are often present in oil and gas wells 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.



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.

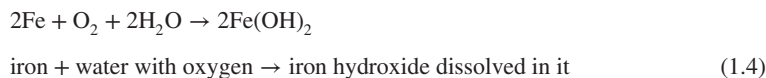


This allows it to bond to other groups of atoms that are negatively charged. We know that wet steel rusts to give a variant of iron oxide, so the other half of the reaction must involve water (H<sub>2</sub>O) and oxygen (O<sub>2</sub>), something like this:

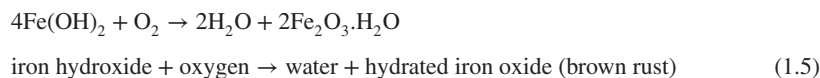


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This makes sense as we have a negatively charged material that can combine with the iron and electrons produced in the first reaction. We can, for clarity, ignore the electrons and write



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



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.



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##### 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



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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



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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.



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### 1.3.1.5 Nitrogen Compounds

Organic nitrogen compounds, such as indole, carbazole, 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  $\text{NH}_3\text{HCN}$ , in combination with  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$ ,  $\text{NH}_3\text{HCN}$ , and small amounts of phenols, mercaptanes, chlorides, and fluorides. High concentrations of ammonia can saturate process water with ammonium bisulfide ( $\text{NH}_4\text{HS}$ ) 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  $\text{H}_2\text{S}$  in refinery flares can produce polythionic acids of the type  $\text{H}_2\text{S}_x\text{O}_y$  (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.

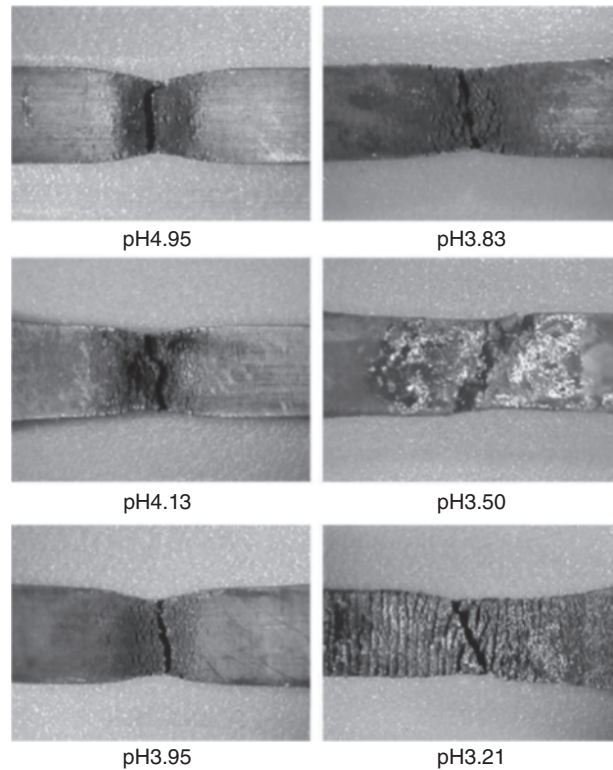
## 1.3.2 Low-Temperature Corrosion by Process Chemicals

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  $1 \times 10^{-7} \text{ s}^{-1}$  at  $150^\circ\text{C}$ . (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  $90^\circ\text{C}$ .

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  $1 \times 10^{-7} \text{ s}^{-1}$  at  $150^\circ\text{C}$ .

### 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).



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### 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.

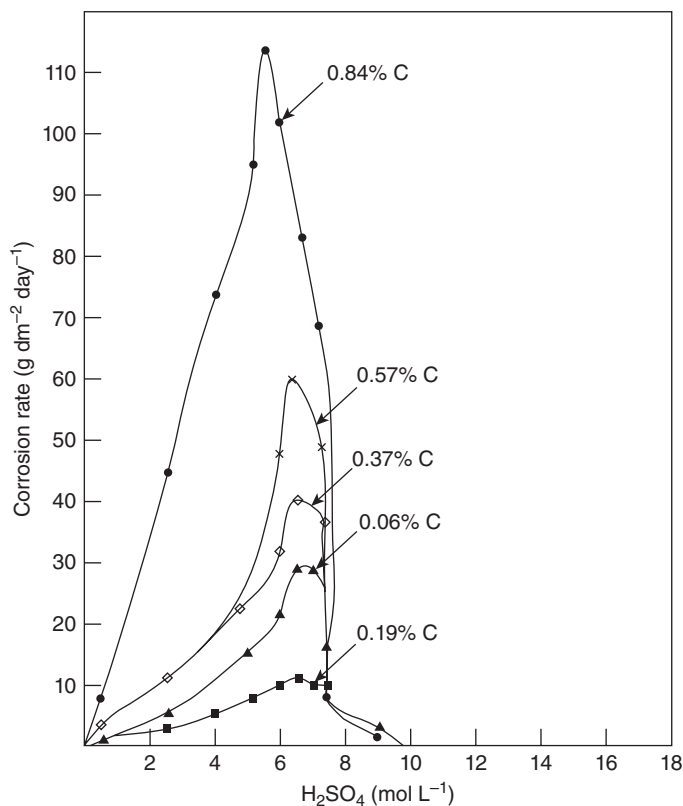
Acid concentrations above 85% by weight are not corrosive to carbon steel if temperatures are below 40 °C. Cold-worked metal (usually used for bends) should be stress relieved. Under ideal operating conditions, few, if any, corrosion and fouling problems occur.

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:  $25 \pm 2$  °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:  $25 \pm 2^\circ C$ . 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  $120^\circ C$ , 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.

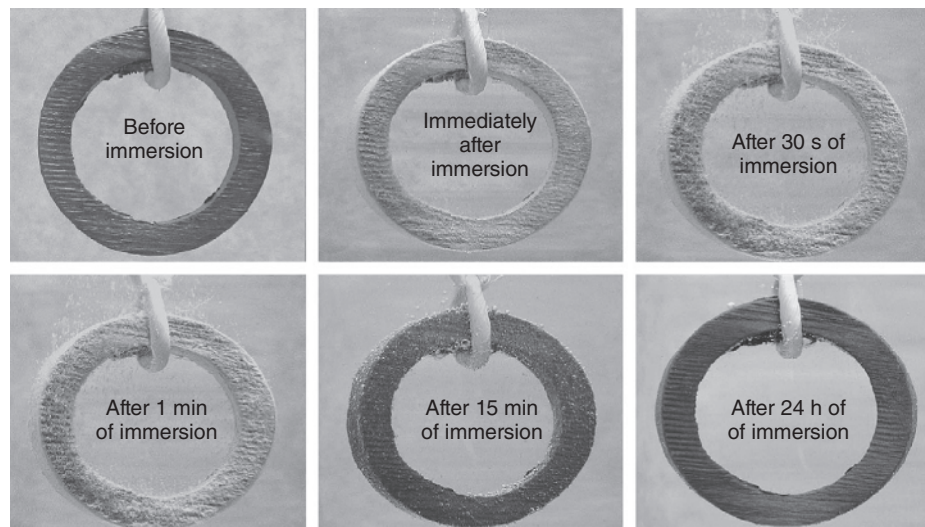
### 1.3.2.7 Amines

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.



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**Figure 1.3** A carbon steel ring in 96% reagent-grade  $H_2SO_4$  under static conditions at  $25^\circ C$  (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
- Sulfidic 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 thinning, 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 converts organic sulfur compounds in feed stocks to hydrogen sulfide; corrosion becomes a function of H<sub>2</sub>S 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.

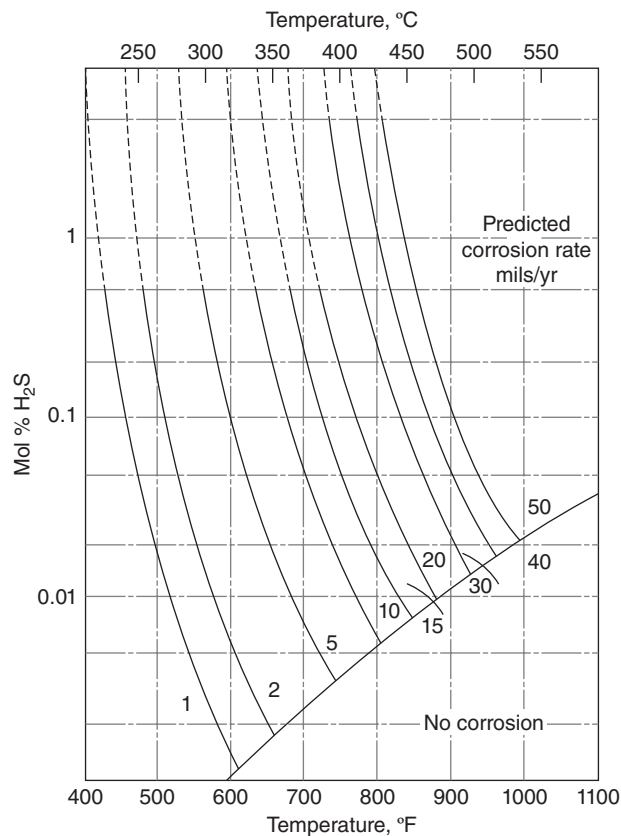
When selecting materials for this service, the recommendations of API 941-2004 should be followed to avoid problems with high-temperature hydrogen attack.

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.



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**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](http://www.wescef.com.au))

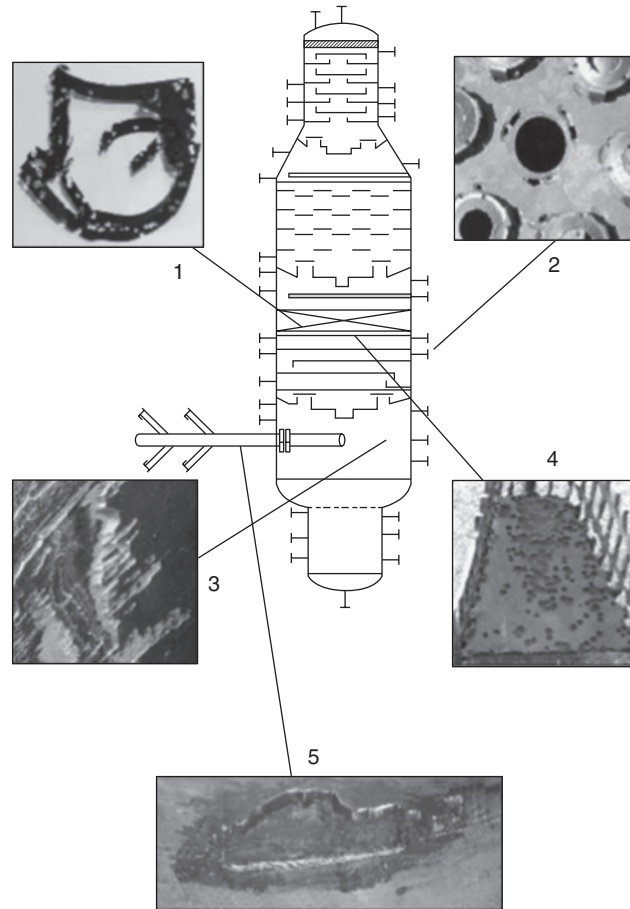
#### 1.4.4 Naphthenic Acids

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.



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### 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 ( $Na_2O \cdot 6V_2O_5$ ). 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.