Corrosion—The Longest War

Locations that host oil and gas operations often provide ideal conditions for corrosion. Ongoing research and advances in coatings, cathodic protection, nondestructive testing, corrosion analysis and inhibitors allow operators to safely produce oil and gas in these corrosive environments.

Corrosion validates the universal law of entropy; everything trends toward a state of greater chaos and disorder. The flecks of rust on an iron bar or the green patina on a copper fixture are evidence of the insidious effects of corrosion. These examples may be regarded as an annoyance, but taken to the extreme, the results of corrosion can lead to catastrophic outcomes.

Corrosion has brought down bridges, downed aircraft, leveled chemical plants, parted drillpipe and ruptured pipelines. Given sufficient time, this adversary has the potential to degrade any material. In certain environments, the unchecked effects of corrosion can come swiftly, and the consequences of failure to manage corrosion can be costly.
According to the US Federal Highway Administration, the approximate annual direct cost of corrosion for the US in 2015 was an estimated US$ 500 billion, representing around 3.1% of the nation’s gross domestic product. This figure amounts to six times the average annual cost of weather-related disasters for the US, which was about US$ 87 billion in 2011. Unlike weather events, corrosion can be controlled or at least managed; scientists estimate that 25% to 30% of corrosion costs could be avoided if good corrosion management practices and preventive strategies were employed.

Throughout the ages, and despite an early lack of understanding concerning the fundamental mechanisms involved, humans have attempted to control corrosion. In ancient times, corrosion resistance was sometimes imparted to materials as a matter of circumstance rather than design (Figure 1). Early corrosion control methods included the use of bitumen and lead-based paints by the Romans in the first century. Around 500 BCE, Chinese sword makers used copper sulfide coatings to inhibit corrosion on bronze swords. Centuries later, the copper sheathing used on British sailing vessels to reduce biofouling fouling of underwater surfaces by organisms such as barnacles and algae—and increase speed accelerated the corrosion of nails that held the ships together.

Michael Faraday was one of the most important contributors to the early understanding of corrosion; in the early 1800s, he established a quantitative relationship between the chemical action of corrosion and electric current. Although much more is known about the subject today, scientists continue to study the mechanisms of corrosion and search for methods to manage and control it.

Combating corrosion is a significant source of expenditures for the oil and gas industry (Figure 2). British Petroleum (BP) conducted a study of its operations in the North Sea in 1995. The company found that outlays for corrosion

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4. The US$ 87 billion cost of weather-related disasters in 2011 was the highest on record. The average annual cost has been closer to US$ 10 billion in recent years. For more on the cost of weather-related disasters: Smith AB and Katz RW: “U.S. Billion-Dollar Weather and Climate Disasters: Data Sources, Trends, Accuracy and Biases,” Natural Hazards 67, no. 2 (June 2013): 387–410.
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This article focuses on descriptions of corrosion, management techniques and advances in corrosion abatement technologies. Field examples from Gabon, deepwater Nigeria and the North Sea illustrate the ongoing battle waged against corrosion by oil and gas operators.

The Corrosion Process

Scientists and engineers today have a better understanding of corrosion processes than did the ancient Romans and Chinese. Fighting corrosion requires an understanding of the principal elements that cause and contribute to the corrosion. There are several categories of corrosion; for the oil and gas industry, common types include exposure to carbon dioxide [CO2, sweet corrosion], hydrogen sulfide [H2S, sour corrosion], oxygen [O2] and corrosion causing microbes, referred to as microbiologically influenced corrosion (MIC).

Some forms of metal corrosion are related to stability; for example, galvanic corrosion is an electrochemical process associated with the movement of electrons between areas that have different electrochemical potentials. The corrosion cell schematically describes oxidizing corrosion, which is analogous to a battery in which two dissimilar metals are connected by an electrolyte (Figure 3). A metal that has a higher corrosion rate—more unstable—represents the negative part of the cell and acts as the anode; a second metal that has a lower corrosion rate—more stable—acts as the positive part of the cell, the cathode.

During the galvanic corrosion process, metal oxides are formed as electrons flow from the anode to the cathode through the electrolyte—the fluid in contact with the anode and cathode. A simplified version of iron oxidation can be used to illustrate the galvanic corrosion process—the actual process is more complex. The presence of water [H2O] on the surface of the iron [Fe or Fe0] releases electrons to form ferrous iron [Fe2+] and ferric iron [Fe3+] ions, which act as the anode in our battery analogy. The liberated electrons flow to the cathode, where, in the presence of oxygen [O2], ferrous oxide [FeO] and ferric oxide [Fe2O3] form as scales of rust or precipitates. A byproduct of the reaction at the cathode is hydroxyl ions [OH−] from the reduction of oxygenated water.

Iron can also react with CO2 to form iron carbonate [FeCO3] and with H2S to form iron sulfides [FeSx]. In the absence of O2 but the presence of CO2 and H2S, the cathodic reaction can generate hydrogen gas.

These reactions can occur rapidly, but if the reaction rate can be reduced, the overall corrosion rate will also be reduced. Many factors influence the reaction rate. These include the type and quality of metal, electrolyte compositions, pH, temperature, pressure, presence of dissolved gases, liquid velocity, water salinity, application of cathodic protection and the presence of microbes. To manage corrosion and corrosion rate, knowledge of the metallurgy of the materials to be used and the environments in which they will operate is important.

If CO2 comes into contact with water in the producing or transportation system of an oil and gas operation, areas typically affected include well internals, gathering lines and pipelines. In CO2 corrosion of iron, the products of reaction are carbonic acid, iron carbonate [FeCO3] and hydrogen gas [H2]. For CO2 corrosion to occur, the partial pressure of the gas can be as low as 21 kPa [3 psi]. To prevent this type of corrosion, operators commonly use organic films that act as barriers and inhibitors that neutralize the acidity of the carbonic acid generated in the corrosion process. Operators may also use corrosion resistant alloys (CRAs), which are resistant to general and localized corrosion, in environments that are corrosive to carbon and low-alloy steels.

Hydrogen sulfide is often found in produced fluids or as a result of MIC. Although H2S is not corrosive, it becomes corrosive in the presence of water. Sour corrosion from H2S can affect any part of the producing system, including well internals and oil and gas gathering lines. Oilfield fluids are considered sour if the produced gas contains more than 5.7 mg of H2S per m3 [4 parts per million (ppm)] of natural gas or produced water has greater than 5 ppm H2S. At the anode, the H2S reacts with the iron to form several variants of iron sulfide [FeSx] such as mackinawite [(FeNi)1−xS], pyrrhotite [Fe1−xS] and trolite [FeS]. These iron sulfide species precipitate and can form localized microgalvanic corrosion cells.

The corrosion cells formed during sour corrosion cause pitting, sulfide stress cracking (SSC) and hydrogen embrittlement. Stress corrosion cracking is a result of tensile stress combined with a wet environment and often causes slow, round pits that have etched bottoms accompanied by branching cracks that can lead to rapid failure. Hydrogen embrittlement occurs when H2S and H2 diffuse into metal, recombine with...
other molecules and create pressure within the metal matrix; byproducts of cathodic protection, galvanic corrosion and other mechanisms may lead to hydrogen embrittlement.

The failure mode during hydrogen embrittlement depends on the steel type; for example, low-strength steels exhibit blistering. The failure mode of high-strength steels can be catastrophic when the pressure of the trapped gas exceeds the tensile strength of the metal. To control sour corrosion, operators use organic film formers, H2S scavengers, metals resistant to SSC, flowline pigs, nitrate treatments and biocides that reduce the growth of microbes that cause MIC.

Oxygen-related corrosion in oil and gas producing environments is often much more aggressive than corrosion caused by CO2 or H2S (Figure 4). Corrosion by oxygen is directly proportional to the concentration of the dissolved gas. If chlorides, CO2 or H2S are present, the corrosion rate can increase significantly.

Oxygen has the ability to induce corrosion throughout producing systems. Inhibition of oxygen corrosion is difficult, and corrosion reduction efforts for production and water handling facilities have usually been directed toward exclusion of oxygen from the system and the use of oxygen scavengers. Typical oxygen scavengers are ammonium bisulfite [NH4HSO3], sodium sulfite [Na2SO3] and sodium bisulfite [NaHSO3]. In addition to scavenger stripping, vacuum deaerators are sometimes used to control the corrosive effects of oxygen on metals.

Exposure to oxygen is also a major source of drillpipe corrosion. While it is being run in and out of the well, drillpipe is exposed to atmospheric oxygen. During drilling, drillpipe comes into contact with oxygen in the mud system. Both instances can induce corrosion. The usual expression of oxygen-related corrosion is pitting. Pitting can even develop under mud left on and inside drillpipe, where pipe storage racks contact the pipe and at crevices. Deep corrosion pits in drillpipe can lead to the onset of fatigue failure. Drillpipe may be coated with epoxies or resins to stop corrosion, but the harsh downhole environment often quickly removes these protective coatings. Pipe dope, lubricating grease applied to threaded connections, may help prevent corrosion of these connections.

**Corrosion Form and Appearance**

The word *corrode* comes from the Latin *corrude* meaning to gnaw; it can carry the additional meaning of eat or wear away gradually. Corrosion typically leaves a visible signature that is characteristic of the agent and mechanism

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**Figure 4.** Corrosion rates. The relative rates of corrosion in milli-inches/year (mpy) of carbon steel show pronounced differences when the steel is exposed to varying concentrations of O2, CO2 and H2S. At a concentration of 5 ppm, O2 is almost three times more corrosive than is H2S and 30% more corrosive than is CO2. Photographs near each curve show the effects of these corrosion agents on metal surfaces.

12. At elevated temperatures, magnetite [Fe3O4] may also form.
13. In MIC, the H2S is produced as a byproduct of the activities of sulfate reducing bacteria (SRB).
18. Pipeline operators send mechanical devices called pigs through pipelines to clean the inner surface. This can be done without halting flow, and the flow stream pushes the pig through the piping.
that caused it. Although not an exclusive list, corrosion usually falls into one or more of the following categories: general or uniform, localized, galvanic, erosion or flow induced, crevice, pitting, under deposit, cavitation, intergranular, stress cracking and corrosion fatigue (Figure 5). Other types of corrosion include environmental, top-of-line and microbial. Based on the observed characteristics of the corrosion, engineers can adopt appropriate preventive and mitigation measures.

**Uniform corrosion** is typical of low-alloy steels and may be observed over an entire exposed area. Initial evidence of uniform corrosion is surface roughness. The metal becomes thinner as the corrosion progresses, and it will eventually fail from internal pressure or external forces. Because this type of corrosion is linked to surface exposure, it may be prevented by properly protecting the surface. Uniform corrosion may occur in equipment used for oilfield operations such as hydraulic stimulation and acidizing.

**Localized corrosion** occurs at specific sites rather than over a generalized area and may be more dangerous than some other types of corrosion because of its unpredictable nature and the potential for rapid growth. Localized corrosion, of which even CRAs such as stainless steels are susceptible, can be subdivided into pitting, crevice and under deposit corrosion. Pitting ultimately can cause holes in metal components and is one of the primary causes of failure in oilfield hardware, including tubing, casing, sucker rods and surface equipment.

**Crevice corrosion** occurs in constricted areas, wherein the metal at the crevice becomes anodic and the rest of the metal serves as the cathode. The crevice can form where two dissimilar metals come into contact or be created by microgalvanic cells that may occur in certain steel alloys.

**Pitting corrosion** rates are often much higher than those of other types of corrosion. Inhibitors may be applied to the surface to prevent initiation, but once a pit has formed the inhibitors are often unable to slow its growth.

**Under deposit corrosion** occurs when sand, corrosives or porous solids adhere to the metal surface. Although the area underneath the deposit is resistant to inhibitors and can corrode quickly, this type of corrosion can often be managed by cleaning internal piping surfaces, for example, with the use of pipeline pigs.

**Galvanic corrosion** can be a problem when two dissimilar metals are in contact. The metal that has the least resistance to corrosion acts as the anode and the more resistant metal serves as the cathode. The anode typically corrodes preferentially. This form of corrosion is frequently observed in offshore platforms and pipelines. The galvanic series, which orders metals according to their anodic or cathodic tendencies, is a good predictor of corrosion severity (Figure 6). Galvanic corrosion is controlled and mitigated by use of the following:

- good engineering design—to ensure that corrosively active components present larger surface area than do less active components
- material selection—to avoid metals far apart in the galvanic series
- isolation—to provide pipelines coming from the sea with sacrificial anodes and protect those going into land with impressed current systems
- inhibitors and coatings—to control initiation of corrosion, although this method may be ineffective once corrosion forms.
Flow-induced corrosion occurs when liquid flow accelerates corrosion. Wellheads and pumps are susceptible to this form of corrosion, which may occur as erosion or cavitation. Erosion corrosion results when fluid flow removes the protective film that forms naturally or has been applied externally. Because of their abrasive properties, suspended solids will accelerate the process. Damage can be seen as grooves in the piping that correspond to the flow direction. Proper engineering design that allows for sufficient pipe diameter and removing solids from flow streams can minimize this type of corrosion. Inhibitors may be applied to replace protective films stripped away by the flowing fluids.

Cavitation is caused by collapsing bubbles that occur when the pressure changes rapidly in flowing liquids. Over time, cavitation may cause deep pits to form in areas of turbulent flow, especially in pump impellers. Low-carbon steels are susceptible; stainless steels are more resilient.\(^2\)

Intergranular corrosion results from corrosive attacks at metal grain boundaries in the form of cracks. The grain boundaries can become anodic with reference to the cathodic surrounding surface, typically due to formation of chromium carbides or nitrides. Metal impurities can increase the effect, as can precipitates in the metal that form during heat treatments. When chromium combines with nitrogen or carbon, less free chrome is available locally for corrosion protection, and cracks can form along the grain boundaries. Quenching—the rapid cooling after heat treatments—may be effective in reducing or eliminating intergranular corrosion. Material selection—avoiding materials that are susceptible to this condition—is the most reliable method to preclude intergranular corrosion. Tests such as ASTM A262 can be used to evaluate susceptibility of materials to this mechanism.\(^2\)

Environmental cracking occurs when corrosion coincides with tensile stress. It may be manifested as the following:

- **hydrogen embrittlement**—hydrogen enters the metal matrix and weakens it
- **stress corrosion cracking**—cracks form after corrosion has attacked a surface
- **sulfide stress cracking**—a failure of the metal caused by \(\text{H}_2\text{S}\).

Material selection—opting for materials that are resistant to hydrogen embrittlement and sulfide cracking—is the primary avoidance technique. Low-stress design practices and stress relief by heat treatment are also commonly used, and preventing corrosion in components subject to stress is another method.

Pipelines are subject to top-of-line corrosion (Figure 7). Water condenses at the top of the pipe as the fluid inside cools. The corrosion rate depends on the condensation rate and concentration of organic acids. Generally, this type of corrosion is controlled with inhibitors and pipeline insulation that reduces condensation.

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Microbiologically Influenced Corrosion

From the moment of immersion in a nonsterile fluid that supports microbial development, microorganisms begin to attach to the material surface (Figure 8). Planktonic microorganisms become fixed at the fluid boundary, typically a pipe wall, or onto porous media such as preexisting corrosion.

Attachment of microorganisms leads to the formation of **biofilms**—microbial communities embedded in or on an attaching surface. Wherever biofilms are found in producing systems, MIC can occur, including inside production tubing, gravity and hydrocyclone separators, storage tanks, pipelines and water injection systems. Depending on the microbial species, the corrosion mechanisms can take various forms.

Biofilms can trap ions and create localized electrochemical potentials analogous to a galvanic corrosion cell or may contribute to corrosion by taking a role in the formation of cathodic and conductive corrosion products on the metal surface (Figure 9). Sulfate producing prokaryotes (SPPs) are the chief offenders. Prokaryotes are microbes that have no cell nucleus or membrane-bound organelles. The most prominent group of SPPs are sulfate reducing bacteria (SRB) and sulfate reducing archaea (SRA). They contribute to corrosion by various means, for example, by taking a role in the formation of cathodic ferrous sulfide corrosion products and the formation of galvanic cells. The production of H₂S by SPPs can also lead to sour corrosion.

Biofilms may develop local concentration cells that are created by oxygen depletion or may attach to a metal surface. Microbes can contribute to corrosion by the direct effects of metabolic waste products such as organic acids that are capable of altering the local pH and forming pH cells. Some microbes are anaerobic and can tolerate extremes of pressure, temperature, pH and fluid salinity. These include methanogens—microbes that produce methane as a metabolic byproduct in anoxic conditions.

Regardless of the source of MIC, prevention measures in most cases attack planktonic and sessile populations. Methods include biocides to kill the microorganisms, coatings to inhibit biofilm formation, removal of nutrients from the flow stream to control microbial populations and mechanical removal of an established biomass via pigging.

Corrosion Control Methods

Metallurgical solutions can be effective deterrents of corrosion, but their costs may be beyond the economic limit of many oilfield projects. Building every structure and tubular from iridium—the most corrosion resistant element—might win the battle against corrosion, but incur unsustainable expenses, and that would be assuming a sufficient supply of iridium exists in the world to attempt such a task. Aluminum is a corrosion-resistant metal used in many oilfield applications; however, it is unsuitable for high-pressure and high-temperature operations. In addition, although aluminum is considered corrosion resistant in seawater, the mechanism for resistance relies on the formation of a thin film of aluminum oxide on the surface of the metal. In environments that have high levels of acidity (low pH) or alkalinity (high pH), the aluminum oxide can become unstable and thus nonprotective. In many cases, steel alloys and CRAs are required to meet both strength and cost requirements.
Although materials selection is a major part of the corrosion control process, once the equipment is deployed, oilfield operations generally follow three methodologies to battle corrosion. Operators and service companies rely on surface coatings to protect susceptible metals, cathodic protection for active protection and inhibitors as a low-cost treatment option.

Surface coatings provide chemical and mechanical resistance. They may also offer thermal protection. For surface coatings to provide maximum effectiveness, good adhesion to the target surface is required. Coatings are available in organic and inorganic types. Organic coatings include epoxies, phenolic resins, polyurethanes, polyethylene and polyesters. Metals applied as suspensions and electroplating are examples of inorganic coatings; inorganic ceramics may also be applied to protect surfaces. Although not normally an advanced-technology solution, the cement placed in the annulus between the wellbore casing and the formation can act as an inorganic coating that prevents corrosion.

Cathodic protection (CP) consists of two primary forms: passive and active (Figure 10). In either form, it relies on a movement of electrons (current) from an external anode to the equipment being protected, which acts as a cathode. Both the cathode and anode must be in the same electrolyte and electrically connected. The most common uses of CP are protecting large structures, piping, casing and equipment exposed to the elements. It may also be installed inside or outside tanks and pressure vessels.

Operators often use sacrificial anodes with CP to protect structures in areas where electrical power sources are not readily available such as in remote operations or on offshore structures. If the structure can be made to serve as the cathode in relation to an anode, the disposable sacrificial anode will corrode while the cathode remains unscathed. This type of CP has been referred to as fighting corrosion with corrosion.27

The first use of CP is attributed to Sir Humphry Davy, who described the process in a series of articles to the Royal Society of London in 1824.28,29 The technique was used in an attempt to prevent the corrosion of nails used in wooden oceangoing vessels. Accelerated corrosion of the nails occurred when copper cladding—used to prevent biofouling—was applied to the outside of vessels. Davy found that sacrificial anodes protected the iron nails. The actual processes were not well understood at that time, but it is recognized today that the contact of dissimilar metals—the copper cladding and the iron of the nails—led to the corrosion. Davy and his assistant carried out a number of experiments on corrosion prevention techniques; that assistant was Michael Faraday, who would later establish the relationship between the chemical action of corrosion and electric current.

In the oil field, CP was first applied to land-based pipelines, and the first documented use was by Robert J. Kuhn in 1928.28 He established a negative 850 mV potential between the steel pipe of a pipeline and a copper-sulphate electrode. This example became the foundation of modern CP technology, although for many years the effectiveness was met with scientific skepticism.

Today, CP uses sacrificial elements made from aluminum, zinc and magnesium to protect the steel of large structures and piping. These dissimilar metals create the galvanic coupling that establishes a current path between the anode and the cathode, and, over time, the sacrificial anode rather than the protected structure experiences metal loss. Appropriate placement and distribution of the anodes is crucial to ensure that all parts of the structure are sufficiently protected.30

Because the direct current (DC) is externally applied, this type of corrosion management is referred to as impressed cathodic protection. It is most frequently used for cases in which the electrolyte resistance is high, such as in soil or freshwater, and where a constant

26. Sessile refers to fixed or immobile organisms.
28. Davy H: “On the Corrosion of Copper Sheeting by Sea Water, and on Methods of Preventing This Effect; And on Their Application to Ships of War and Other Ships,” Philosophical Transactions of the Royal Society of London 114 (January 1, 1824): 151–158.
source of current is readily available. The use of solar panels in remote locations has greatly increased the potential applications of impressed cathodic protection.

In the impressed CP technique, current of several amps from a low-voltage rectifier passes, or is impressed, from an inert anode (for example, graphite or iron) to the structure being protected, which acts as the cathode. The anode is attached to the positive terminal of the DC source, and the cathode is attached to the negative terminal. The anode and cathode are often some distance from each other, separated by an electrolyte.

To counteract corrosion, sufficient current density must be supplied to all parts of the protected structure and the current density must always exceed what would be the measured corrosion rate under the same conditions. If the corrosion rate increases, the impressed current density must be increased. Although the initial equipment cost may be higher for impressed CP than it is for sacrificial protection, this technique may be less expensive over the long term because sacrificial anodes do not need to be replaced. Impressed CP also has the advantage of providing information to the operator about the extent of corrosion over time.

**Corrosion Inhibitors**

Another line of defense against corrosion is inhibitors, of which there are a variety of types and applications. The primary goal of inhibitors is to interrupt the electrochemical process by which the corrosion cell forms between the metal and the liquids in and around the equipment. Inhibitors can be a flexible and cost-effective method of fighting corrosion, and the inhibitor application can be altered when conditions change. Although acquiring and delivering the inhibitor incur an ongoing cost, the lower costs associated with using less corrosion resistant low-carbon steels usually more than make up the difference.

Inhibitors fall into four main categories: scavengers, reactive agents, vapor phase and film formers. **Oxygen scavengers** are frequently used in operations in which oxygen poses a corrosive threat. These agents not only reduce oxidizing corrosion, but also control the growth of microbes that require oxygen to thrive. Examples of oxygen scavengers used in the oil and gas industry are sodium sulfite, sulfur dioxide, sodium bisulfite, sodium metabisulfite and ammonium bisulfite. Ammonium bisulfite and sodium bisulfite are commonly used in seawater injection systems. To speed reaction rates, a catalyst may be included in the chemical.

**Hydrogen sulfide scavengers** reduce the level of H$_2$S in the flow stream. Examples of H$_2$S scavengers are amines, aldehydes and zinc carboxylates. Common forms of amines are monoethanolamine (MEA) and monomethylenamine (MMA) triazine. In some situations, operators may be able to regenerate MEA and MMA for reinjection and reuse.

**Reactive inhibition** operates at the cathode level for the corrosion cell. The cations of the inhibitor react with the cathodic anions to form insoluble films, which adhere to the surface of the metals and prevent O$_2$ from coming into contact with the metal. These films also prevent the evolution of H$_2$, a byproduct of the corrosion cell. Examples are forms of calcium carbonate, magnesium carbonate and iron oxides. Reactive inhibitors can also serve as poisons to the corrosion cell process by interfering with the formation of H$_2$ and reducing the reaction rates at both the cathode and anode.

**Vapor phase inhibitors** are primarily used for combating CO$_2$ corrosion. These inhibitors neutralize CO$_2$ and block the formation of carbonic acid [H$_2$CO$_3$]. They are transported via vapor phase in wet gas lines. To protect against future corrosion, they may also be used during hydrostatic testing of components with water, especially when the components are to be stored after fitness testing. Examples of these types of inhibitors include morpholine and ethylenediamine.

**Film Formers**

Film formers are the most widely used corrosion inhibitors in the oil and gas industry. They create a continuous layer between the metal and the reactive fluids, thus reducing the attack of corrosive elements (Figure 11). They may also attach to the surface of corroded metal, altering it and reducing the corrosion rate. Although they are effective in reducing CO$_2$ and H$_2$S corrosion, film formers are not effective against O$_2$ corrosion.

Film formers are available in oil-soluble, water-soluble and oil soluble–water dispersible forms. **Oil-soluble inhibitors** are used to treat oil- and gas-producing wells. **Water-soluble inhibitors** are used in high water-cut flow streams, including those found in producing wells, transmission lines and separators. **Oil soluble–water dispersible inhibitors** are used in oil and gas wells that are also producing water.

Film-forming inhibitors take various chemical forms but are typically composed of long carbon chains with nitrogen, phosphate esters or anhydrides. Inhibitors may adhere to or be adsorbed on the metal surface, which prevents the corrosives from attacking the metal. The most effective film-forming inhibitors create a molecular bond at the metal surface in a process of charge sharing or charge transfer. For effective inhibition, the surface of the metal being protected must be fully covered; injection of the proper concentrations of the inhibitor are crucial. After they interact with the corrosive elements, some
inhibitors are gradually removed from the metal surface and must be continuously replenished with new inhibitor.

In the petroleum industry, organic inhibitors are frequently used because they can form protective layers even in the presence of hydrocarbons. Amides and imidazolines are examples of organic film-forming inhibitors that are effective over a wide range of conditions, especially in sweet (CO₂) and sour (H₂S) gas corrosion environments. They can be water or oil soluble. Amines, which are also organic inhibitors, are effective for sweet and sour corrosion but may exhibit biologic toxicity and are thus not as environmentally friendly as are amides.

Quaternary ammonium salt, or quaternary amine, inhibitors are effective against sour corrosion. The corrosive element formed by sour gas is iron sulfide on the metal surface. Quaternary ammonium cations, or quats, are positively charged, and when they are adsorbed on the surface of the material to be protected, they disrupt the normal corrosion cell charge. However, at least one study indicated that quaternary ammonium inhibitors may actually increase the corrosion rate of sweet corrosion in the presence of brine. The biocide properties of quaternary ammonium salts may also prevent MIC.

Many additional film formers are used in the oil and gas industry, including phosphate esters, ester quats, dimer and trimer acids and alkyl pyridine quaternary compounds. Most film-forming applications include multiple inhibitors; laboratory testing is used to establish optimum concentrations, fluid tolerances, stability, effectiveness and persistency of the film. Inhibitor selection can be a complicated process and typically must be adjusted over time to meet the demands of changing fluid conditions.

Inhibitor Selection

Laboratory evaluation is the key to developing an effective program in inhibitor selection for corrosion control. Technicians begin the process using fluid samples that replicate field conditions—actual produced fluids are best if available. Simulated and synthetic fluids are used when produced fluids cannot be obtained. From laboratory tests, corrosion rates can be measured and predictions can be made for large-scale operations (Figure 12). Methods for testing corrosion inhibitors include the following tests: wheel, kettle (also called linear polarization resistance (LPR) tests), rotating cylinder

![Figure 12. Laboratory testing of corrosion inhibitors. Operators usually develop corrosion control plans and then test inhibitors using conditions expected from the field. This flowchart follows a testing sequence. Three common testing methods are the rotating cylinder electrode, kettle and autoclave tests (middle). Even after laboratory testing, field trials should be conducted to validate the effectiveness of the program. A sidestream test (lower left) acquires samples for analysis. If the proposed method provides acceptable results, the method is adopted, although the corrosion inhibition program must be reevaluated during the life of the well.](image)

electrode, autoclave, jet impingement and flow loop (Figure 13). The most common are the wheel and kettle tests.

The wheel test measures the loss of metal during a specified period of exposure to corrosive liquids. Corrosives include produced fluids, brines and refined oils. The test fixture includes a rotating wheel inside a sealed box that keeps the specimen, usually strips of metal or coupons, in constant motion. Temperature can be maintained at a constant value or varied to simulate field conditions. The samples are tested with and without inhibitor and the results are compared.

The kettle test, or LPR test, measures corrosion rates electrochemically. Metal electrodes are placed in the test vessel, which is heated while the corrosive fluid is continuously agitated. Agitation attempts to replicate field conditions—mild agitation is similar to flow of two distinct sources, and high agitation replicates turbulent fluid flow that has dispersed hydrocarbons. To simulate the presence of gases, CO2 and H2S can be bubbled through the liquid in the vessel in a process referred to as sparging.

To establish a control corrosion rate, the test is run with the electrodes exposed to the fluids in aqueous phase without an inhibitor and then followed by a series of tests on solutions that have increased inhibitor volumes. Linear polarization is performed by controlling the voltage potential and measuring the current then controlling the
current and measuring the voltage potential. The data are plotted, and the slope of the line is the polarization resistance, which is inversely proportional to the corrosion rate (Figure 14). This technique provides corrosion rate evaluation from external measurements, whereas other methods require technicians to physically measure and evaluate corrosion.

The effectiveness of inhibitors is dependent on fluid velocity. For fluids containing little or no solid particles, high flow rates can lead to flow-accelerated corrosion. If the flow stream contains solid particles, the accelerated corrosion is termed erosion corrosion. Several test methods have been developed to model corrosion in high-flow conditions and determine a film’s persistence, especially where turbulent flow is present. Test methods include jet impingement, rotating cylinder electrodes and flow loop testing.

The testing of inhibitors should determine the following:

- thermal stability
- emulsification tendency
- foaming tendency
- metal compatibility
- elastomer compatibility
- compatibility with other chemicals used in the same stream.

Application methods should be evaluated as well. Injection may be continuous, batch or squeeze. The rate of film removal is a key concern when determining the optimal application mode.

**Corrosion in the Oil Field**

A recent example of pipeline corrosion from Gabon illustrates the need for thorough testing and understanding of the corrosion process. A pipeline transports oil from the Rabi field to Cape Lopez—a distance of approximately 234 km [145 mi]. The 18-in. pipeline comprises three sections: Section 1 from Rabi to Batanga, 105 km [65 mi]; Section 2 from Batanga to Tchengué, 100 km [62 mi] and then Section 3 from Tchengué to Cape Lopez, 29 km [18 mi] (Figure 15).

The inlet pressure at Rabi was about 40 bar [580 psi], and the flowing temperature was 60°C [140°F] at the inlet. Beyond the inlet, the line operates at about 35°C [95°F]. Impressed cathodic protection is used for the pipeline, which has sections that have solar cells to provide current. The pipeline was coated with three-layer polyethylene; each joint was brush cleaned and wrapped with heat-shrink.
sleeves and hot-melt adhesive that overlapped the polyethylene. The pipe was buried in wet, compacted sand that had a pH of approximately 5.4.

Problems began to develop in the first 15 km [9.3 mi] of pipe. Routine inspections found disbondment at the sleeves where they overlapped the polyethylene coating in the Rabi section. Disbondment allowed water under the protective coating, which negated the cathodic protection and allowed corrosion to develop (Figure 16). The remainder of the pipeline did not experience the same level of corrosion, although significant disbondment occurred in the sleeves. The main difference between the sections that had differing corrosion levels was that the temperature in the more corroded sections was higher. Further testing of pipe Sections 2 and 3 found no evidence of similar levels of disbondment or corrosion.

After a thorough examination, engineers recommended abrasive blast cleaning prior to applying heat-shrink sleeves for future installations rather than the standard brush cleaning of connections. Another possible solution was liquid polyurethane or epoxy applied at the joints. The disbonded coating may have prevented cathodic current from reaching and protecting the surface of the exposed steel. Although engineers discovered corrosion as a result of disbonding of coatings, based on ASME standards, the degree of corrosion was deemed not mechanically dangerous. They also concluded that as long as coatings remain bonded to the steel and cathodic protection is correctly applied, monitored and maintained, no corrosion risk existed for this pipeline.

**Corrosion Inhibitors in Deepwater**

Deepwater projects can pose unique challenges for corrosion control because the completions are usually located at the seafloor and flowlines must come to the surface or back to shore. A deepwater field located in the southern Niger delta demonstrates the use of inhibitors to combat CO₂-induced corrosion (Figure 17).

The production path for deepwater wells passes through cold water, which can subject the originally hot fluids in the flow stream to rapid cooling. Conversely, inhibitor injection is often through long umbilicals that are subjected to temperature contrasts between the surface and subsea wellheads. Injection of inhibitors is further complicated by the normally high flowing pressures associated with deepwater production.

Temperature extremes, pressure extremes and long umbilicals combine to affect inhibitor...
stability, performance and properties. Thorough testing of the inhibitors is required to ensure corrosion controlling properties are maintained, that the injected chemicals remain stable and that the inhibitors can be reliably delivered via the umbilicals into the flow stream.

Another risk in deepwater production is the formation of hydrates—ice-like solids of water and gas that form above the normal freezing point of water—that can plug flowlines. To ensure corrosion controlling properties are maintained, inhibitors must be thoroughly tested to confirm that the injected chemicals remain stable and that the inhibitors can be reliably delivered via umbilicals into the flow stream.

These conditions were faced by an operator of a deepwater production platform in Nigeria. The platform served nine wells drilled in water depth of 1,030 m [3,380 ft]. The operator used subsea completions that included five manifolds and eight production flowlines and risers. The flowlines were connected to a floating production, storage, and offloading (FPSO) vessel that had 320,000 m³ [2 million bbl] of onsite storage capacity. Produced oil flowed to the FPSO for transfer to tankers. Produced gas was directed to the umbilicals.

The pipelines used to transport the oil and gas were constructed of carbon steel. The flowing pressure from the wells averaged 80 bar [1,160 psi], and the average temperature was 85°C [185°F]. The water cut was 45% and the natural gas contained about 1.4% CO₂. The combination of produced water (brine) and CO₂ presented a high corrosion-rates potential for the low-carbon steel. In wet gas pipelines such as these, produced water has a tendency to condense at the top of the pipe, allowing top-of-line corrosion; the presence of both water and CO₂ accelerates corrosion.

Engineers installed chemical umbilicals of 1 to 20 km [0.6 to 12.4 mi] to inject corrosion inhibitor into the deepwater production flowlines. As the project progressed, engineers at M-I SWACO, a Schlumberger company, reevaluated the initial inhibitor used in the project, which also protected the topside piping and storage vessels, and deemed it to be insufficient.

Engineers developed the DS-1617 deepwater corrosion inhibitor to meet the challenges of this facility. To qualify this inhibitor, they tested the chemicals in accordance with the API TR 17TR6 standard, which requires replicating the temperatures and pressures experienced by the inhibitor during deployment through the umbilicals. The evaluation included high-pressure flow-loop stability tests. The engineers conducted additional tests to look at resistance to hydrate formation, thermal aging and compatibility with seawater. Because the operator was concerned about foaming in the glycol regeneration unit, the inhibitor was tested for foaming tendency.

Laboratory technicians performed kettle tests using the DS-1617 inhibitor at 20 ppm, which is a relatively low dosage; the corrosion rate was reduced by 99% (Figure 18). They also performed high-temperature autoclave testing on carbon steel coupons. The samples were subjected to test fluids that had corrosion inhibitor and to pressurized CO₂ heated to 120°C [248°F]. The results indicated a 98% reduction in the corrosion rate. The 20 ppm concentration yielded corrosion rates of about 0.00016 in./year [0.004 mm/year]. For corrosion rate, the standard industry units are milli-inches/year, or mpy. For this test, the corrosion rate was equivalent to 0.16 mpy. Test technicians reported no foaming problems associated with the inhibitor.

The operator adopted the use of the DS-1617 inhibitor and monitored corrosion at six locations on the FPSO. No corrosion monitoring was installed on the deepwater flowlines. The DS-1617 inhibitor was injected at a 100-ppm rate, which is a lower rate than the initial inhibitor that was deemed insufficient. Criteria for corrosion protection established by the operator was a rate below 0.05 mpy [0.0025 mm/year]. Testing at all six locations indicated corrosion rates below the target rate (Figure 19). Based on the testing, the operator implemented the use of the DS-1617 inhibitor.

Figure 18. Corrosion testing of the DS-1617 inhibitor. Technicians conducted kettle tests with fluids representative of field conditions to evaluate the effectiveness of the DS-1617 inhibitor (top). They also performed autoclave testing at high temperature (bottom). The corrosion rate is in milli-inches of penetration/year (mpy).

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Dose Rate, ppm</th>
<th>Uninhibited Corrosion Rate, mpy</th>
<th>Inhibited Corrosion Rate, mpy</th>
<th>Protection, %</th>
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<tbody>
<tr>
<td>DS-1617 inhibitor</td>
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<td>173.01</td>
<td>4.18</td>
<td>97.58</td>
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<tr>
<td>DS-1617 inhibitor</td>
<td>20</td>
<td>156.43</td>
<td>0.98</td>
<td>99.37</td>
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Figure 19. Corrosion monitoring at a production facility. The operator injected DS-1617 inhibitor into the flowlines of producing wells using underwater umbilicals. The corrosion rate of the flowlines was monitored at the low-pressure separator A (blue), low-pressure separator B (red) and the bulk oil treater (green) as well as at three other locations (not shown). The corrosion rate dropped below the target level (black) established by the operator. Corrosion rates remained below the threshold at all test sites for the duration of the testing period.

North Sea Cathodic Protection

North Sea production platforms routinely use cathodic protection. On one platform, the operator installed 10 sacrificial anodes below the surface of the water and left them in place for eight years. The anodes were composed of zinc, silver and silver chloride and were located at various depths and locations on the platform. The system was designed to protect the structure for a minimum of 20 years. Engineers monitored the output current from three of the anodes over the period. The anodes were removed and inspected at the end of eight years.

After retrieval, the sacrificial anodes were cleaned and weighed (Figure 20). Technicians determined changes in physical dimensions and measured electrical properties. Four anodes were analyzed for the study. The reduction of anodes that had been placed in deeper water was greater than that of those placed in shallower water. Some of the anodes were so corroded that visual inspection was difficult (Figure 21).

The original 20-year design projected that at eight years, the anodes should be reduced by 40%; however, the average weight loss of the anodes was only 24%. The engineers concluded that the original design, although conservative, would protect the structure for at least 20 years. Based on the results of the study, a model was established for periodic inspections to be performed.

New Developments in Corrosion Control

Controlling corrosion has been an ongoing battle between humans and nature for millennia. Since scientists such as Sir Humphry Davy and Michael Faraday discovered some of the underlying physics that explained corrosion, various methodologies have been adopted and adapted. Modern scientific understanding and new technologies are combining to improve the tools available to fight the unending battle with corrosion.

One area of emerging materials science is nanoparticles and nanostructures. Having surface thickness of 1 to 100 nm, these coating materials have unique properties that may make them almost impervious to corrosion. Nanoparticles and nanostructures may be deposited on metal surfaces as films, similar to film-forming techniques, but because of nanoparticles’ greater persistence, reapplying them is unnecessary. The surfaces also become super-slick—exhibiting low friction coefficients—which reduces wear and increases durability. Such surfaces are also less likely to experience biofouling.

The battle against corrosion will never be won; entropy will eventually win the war. Humans will, however, continue to search for effective means to combat this nemesis. The costs of ignoring the problem are too great and the consequences of failure can be potentially catastrophic. At least in the oil field, operators are armed with knowledge, science and effective tools that allow them to actively manage or mitigate the effects of corrosion. —DEA/TS

### Table

<table>
<thead>
<tr>
<th>Anode</th>
<th>Water Depth, m</th>
<th>Weight Loss, %</th>
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<tr>
<td>1</td>
<td>13</td>
<td>13</td>
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<tr>
<td>2</td>
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<td>4</td>
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<td>39</td>
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**Figure 20.** Anode corrosion after eight years of service in the North Sea.

**Figure 21.** Cathodic protection on a North Sea platform. Anodes were recovered after eight years of service from a North Sea platform. After the anodes were cleaned and weighed, technicians were able to determine the effectiveness of the anodes at protecting the structure.

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