

Introduction

Corrosion costs the oilfield millions of dollars each year. A large portion of this expense is due to the replacement of steel goods. Other expenses include lost drilling time due to equipment repairs, fishing operations and extra trips caused by corrosion-related failures. Many wells have to be redrilled due to drill pipe and casing failures caused by corrosion.

All drilling fluid corrosion problems cannot be eliminated, but most can be controlled with proper diagnosis and treatment. This chapter discusses the basics of the corrosion process — corrosive agents, corrosion factors, corrosion inhibitors, corrosion scavengers, and the methods of detection and measurement of the various forms of corrosion.

Fundamentals

Corrosion is the deterioration of a substance or its properties...

THE CORROSION PROCESS

“Corrosion is the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment.” See “*Corrosion Basics – An Introduction*,” NACE International.

Although it may seem that corrosion occurs indiscriminately, there are actually four components which must be present for the corrosion process to take place. The four components necessary for corrosion are: (1) an anode, (2) a cathode, (3) an electrolyte and (4) a conductive path.

To understand these four components better, compare them to a common flashlight. The flashlight’s dry cell battery uses internal “galvanic” corrosion (corrosion caused by the connection of conducting materials that have different electrical potentials) to generate external electrical power. The dry cell battery has a zinc case (anode) which is isolated from a graphite or carbon center (cathode) by a corrosive electrolyte. When the zinc case is electrically connected to the carbon (graphite) center through the light bulb by an external electrical path, current flows lighting the bulb.

Corrosion

components

Anode	Negative pole
Cathode	Positive pole
Electrolyte	Conductive salt medium
Metallic path	External circuit

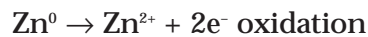
Battery

equivalent

When the circuit is closed, current flows from the cathode to the anode through the connecting circuit and bulb. Inside the battery, current flows from the anode to the cathode through the electrolyte. In any corrosion cell, corrosion (metal loss) always occurs at the anode and current flows **from** the anode **through** the electrolyte **to** the cathode.

In the dry cell battery, zinc is the anode, carbon is the cathode, and the electrolyte is ammonium chloride and zinc chloride. A small quantity of manganese dioxide is mixed into this electrolyte to depolarize the cathode (remove the hydrogen), allowing current to continue to flow when connected. The zinc anode dissolves and ionizes to Zn^{2+} , releasing two electrons ($2e^-$) causing current to flow.

1. Anode reaction:



2. Cathode reaction:

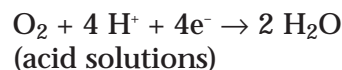


With iron (Fe), a similar oxidation reaction occurs:

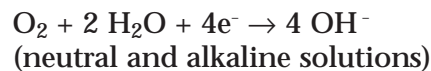


There are several other cathodic reactions encountered during the corrosion of metals. The following should be considered:

Oxygen reduction:



Oxygen reduction:



Hydrogen evolution $2 \text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow$

Metal Ion reduction $\text{Fe}^{+3} + e^- \rightarrow \text{Fe}^{+2}$

Metal deposition $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0$
(copper metal)

To stop corrosion in the battery example, the flow of current must be stopped. Disconnecting the bulb is one way to stop the reaction, but interrupting the anodic reaction or cathodic reaction and isolating the electrolyte or metallic path are other ways to stop corrosion.

In drilling and completion fluids situations, the “wet”-type corrosion processes is the major problem. Wet corrosion has two reactions occurring simultaneously, one at the anode and one at the cathode. These reactions are totally dependent upon each other. The corrosion process can be controlled by disrupting either reaction.

With drill pipe, casing, tubing, etc., corrosion can occur in a way similar to that of a battery. Anodes and cathodes exist on the same piece of pipe and are connected through the metal.

When the pipe is placed in a conductive environment (drilling fluid), corrosion can occur. Corrosion cannot be completely stopped in water-base drilling, workover and packer fluids, but it can be reduced to an acceptable level. To completely stop corrosion, the drilling fluid would have to be completely non-conductive, or the pipe would have to be completely insulated by a protective film (corrosion inhibitor) or coating. These are not practical options in a hostile drilling environment. Changing the metallurgy to a more corrosion-resistant alloy or to one that

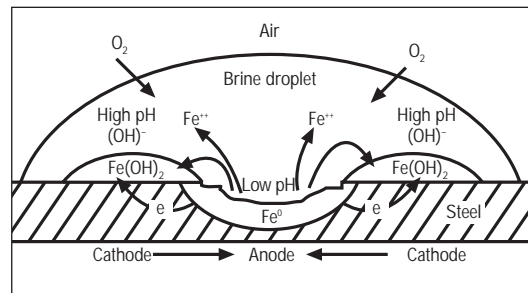


Figure 1: Corrosion at pipe surface.

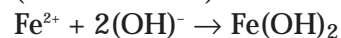
is not as susceptible to the particular type of corrosion being experienced will also reduce the corrosion rate.

The corrosion reaction in drilling fluids can be understood by analyzing and visualizing the two reactions that take place, as illustrated in Figure 1. At the anode, iron (Fe^0) reacts with the electrolyte (dissolves), ionizes to Fe^{2+} and releases two electrons ($2e^-$):

Anode reaction:



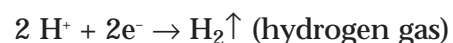
(iron dissolves)



(dissolved iron forms iron hydroxide)

The electrons flow through the metal to the cathode, where two reactions occur, the first produces hydrogen gas:

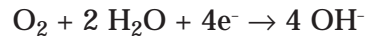
1st cathode reaction:



Wet corrosion has two reactions occurring...

The second cathode reaction involves dissolved oxygen and readily occurs in drilling fluids:

2nd cathode reaction:



Hydrogen evolution and oxygen reduction are the most common cathodic reactions. If any of these reactions can be eliminated or slowed down (controlled), then the corrosion rate will be slowed.

Dissimilar materials have differences in electrical potential. Their union creates the potential for current to flow. This electrical potential or voltage exists between the anode and the cathode. In a conductive liquid (electrolyte), the metallic path completes the electrical circuit and allows current to flow back to the anode.

The electrical potential refers to the potential energy that is stored in the metal. During the refining of metal ores, energy is stored in the metal. This energy is released during the corrosion process. The corrosion of refined metals is a natural process wherein they react to form more stable, lower-energy-level states until eventually they return to their original natural state (ore).

For example, iron (Fe^0) is most stable as an iron ore, represented as Fe_2O_3 . When iron ore is refined, tremendous amounts of energy in the form of heat are required. The refined iron now has potential energy stored. Corrosion is the release of this potential energy as the metal (iron/steel) tries to return to its lower-energy, more stable state.

The amount of energy stored in the metal is known as the metal's *potential*. Different metals require different amounts of energy to refine and therefore have different tendencies to corrode. The greater the amount of energy required to refine a metal, the greater the tendency to corrode. For example, iron has a much greater tendency to corrode than gold. Gold ore is found in

nature as an almost pure material and is refined with ease, requiring little energy.

Differences in potential drive the corrosion reactions. In the dry cell, the zinc metal is the anode, and the graphite/carbon is the cathode. Zinc requires more energy to refine from an ore than carbon. Therefore, zinc has the greater potential, making it the anode. Remember, the "*Action is at the Anode.*" The cathode does not corrode.

While it may be simple to determine the anode and cathode when corrosion involves two dissimilar metals, drill pipe corrosion occurs even though it is supposedly one homogeneous metal. The differences in potential that exists on drill pipe are more subtle than the differences between two different high- and low-energy metals.

Certain impurities and stresses exist in drill pipe and serve as sites where anodes may develop. Also, any changes in the pipe's surface such as nicks, pings (from hammers) or notches (from tongs or slips) may set up stressed areas for corrosion cells which make these areas more susceptible to cracking. Even small differences in the electrolyte in contact with the pipe may set up cells.

TYPES OF CORROSION

Here is a list with short definitions of the most common types of corrosion:

General corrosion. Corrosion which is uniformly distributed on the metal surface. This happens when localized areas, or cells, become polarized, forming anodes and cathodes. These areas are as small as the individual grain structure of the steel. Metal loss occurs at the anode. When corrosion by-products (rust) deposit on the surface of the metal, the potential of the cells reverses and the cathodes and anodes shift until further deposition causes the potential to reverse again. This kind of corrosion is commonly reported in weight loss units of "*pounds per square foot per year*" ($\text{lb}/\text{ft}^2/\text{yr}$) or "*mils per year*" (mpy).

The electrical potential refers to the potential energy...

The amount of energy stored in the metal is known as the metal's potential.

Pitting occurs when the anodes and the cathodes do not shift...

In the field, $lb/ft^2/yr$ units are used, while laboratory evaluations use *mpy*. Uniform corrosion is usually the least damaging form of corrosion because it is spread out over the entire surface area of the pipe.

Pitting corrosion. Highly localized corrosion confined to a small area which takes the form of pits or cavities. Pitting occurs when the anodes and the cathodes do not shift; the area of the pit is anodic. As the anode corrodes away, pitting deepens, and holes or deep cracks result. Pitting is often seen in the damaged slip area of the drill pipe. When pitting attack occurs, if the corrosion rate is expressed as $lb/ft^2/yr$ or *mpy*, it is somewhat misleading because the corrosion is concentrated in only a few small places representing only a small fraction of the surface area of the pipe.

Crevice corrosion. Localized corrosion resulting from the formation of a concentration cell in a crevice formed between a metal and a nonmetal or between two metal surfaces.

Stress Corrosion Cracking (SCC). Corrosion resulting in cracking caused by the combined action of tensile stresses and a corrosive environment. Acting alone, neither the tensile stresses or corrosive environment would cause cracking. Stress corrosion has serious consequences since failure can occur at stress levels below the physical properties of the metal and mechanical design limits of the pipe.

With stress corrosion cracking, most of the steel surface is not affected, and little corrosion appears to be taking place. Most often, SCC begins at the base of a pit, reducing the strength of the metal at this point. Subsequent stress will propagate the crack, allowing fresh metal to be exposed to the corrosive environment. This results in continued corrosion, weakening and eventually failure. The process occurs so rapidly that there may be very little generalized corrosion.

...failure can occur at stress levels below...

A common example of SCC is a washout in the fade-out of the upset of drill pipe. (The upset is the transitional portion of the drill pipe between the drill pipe tube and tool joint. It is where the wall thickness increases for the last few inches of the drill pipe tube to give extra area (strength) for welding the tool joint to the tube. The fade-out is the transition where the upset returns to the tube's normal thickness.) While drilling, the drillstring is often bending as it is being rotated, causing cyclic tension and compression stresses. These bending forces acting through the tool joints are concentrated at the fade-out of the upset. The tensile stresses (stretching) cause transverse cracks exposing more reactive steel to attack by oxygen corrosion. Oxygen scavengers and passivating inhibitors such as CONQOR® 404 can help control this problem, but additional washouts from pre-existing pits and cracks can be expected for several days after treatment is started.

Sulfide Stress Cracking (SSC). Brittle failure of high-strength steels by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. This failure is catastrophic and can occur without warning.

Concentration cell. Corrosion caused by exposure to different ionic concentrations, also called *shielding* or *underdeposit corrosion*. It occurs under dried mud, pipe scale or pipe protector rubbers where "concentration cells" are formed. Casing is subject to external concentration cell attack when exposed to formations in close proximity that have significantly different salinity.

In the drilling operation, if mineral scale or mud solids adhere to the pipe surface, the metal directly below this scale can corrode. This sets up a concentration cell as the pipe is exposed to a different environment than the rest of the metal pipe surface. With

Erosion results from movement of a corrosive fluid on a metal surface.

dissolved oxygen in the mud, the area under the deposit will “see” a lower oxygen concentration and start pitting in that area. A similar cell can occur under drill pipe protector rubbers. Moving the rubbers will help move the location of the attack, but will not stop the reaction. This type of attack under the drill pipe protector rubbers causes pitting which looks like a groove around the drill pipe. These types of corrosion cannot be controlled with filming amine corrosion inhibitor treatments, but can be controlled with oxygen scavengers and/or passivating inhibitors such as CONQOR 404.

Erosion corrosion. Erosion results from movement of a corrosive fluid on a metal surface. High velocities or the presence of suspended solids can lead to erosion corrosion. Constantly removing or eroding any passive film on the metal may leave its surface bare and susceptible to corrosion.

Intergranular corrosion. A form of localized surface attack in which a narrow path is corroded preferentially along the grain boundaries of a metal.

Corrosion fatigue. Failure of a metal by cracking when it is subjected to high cyclic stresses. The endurance limit is a stress level below which no failure should occur, even with an infinite number of cycles. Corrosion fatigue is characterized by much shorter life than would be expected as a result of either the mechanical stresses or chemical corrosive environment alone. It is typically evident as washouts in drill-string components which experience high bending stress.

Dealloying. A localized type of corrosion that involves the selective removal (i.e., corrosion) of one of the elements of the alloy. This is also called *parting*.

Galvanic corrosion. Galvanic cell corrosion (bimetallic) refers to corrosion which results from two joined, dissimilar metals being immersed in a conductive medium. A potential difference exists between dissimilar metals. When they come into contact, this potential difference causes electrons to flow from one metal to the other causing corrosion. In this galvanic couple, each metal reacts differently than when it is freely corroding. The anodic metal corrodes more rapidly and the cathodic metal corrodes little, if at all.

Since a galvanic couple protects the cathodic metal, it is possible to protect one metal from corrosion by placing it in contact with a dissimilar metal which has higher potential energy. The higher potential metal (usually Mg, Al or Zn) becomes the sacrificial anode, and the protected metal is the cathode. The practice is known as *cathodic protection*.

The tendency of each metal to corrode must be examined to determine which metal will corrode in a galvanic couple. Generally, the less corrosion-resistant metal becomes anodic to the more corrosion-resistant metal (cathodic) which becomes protected.

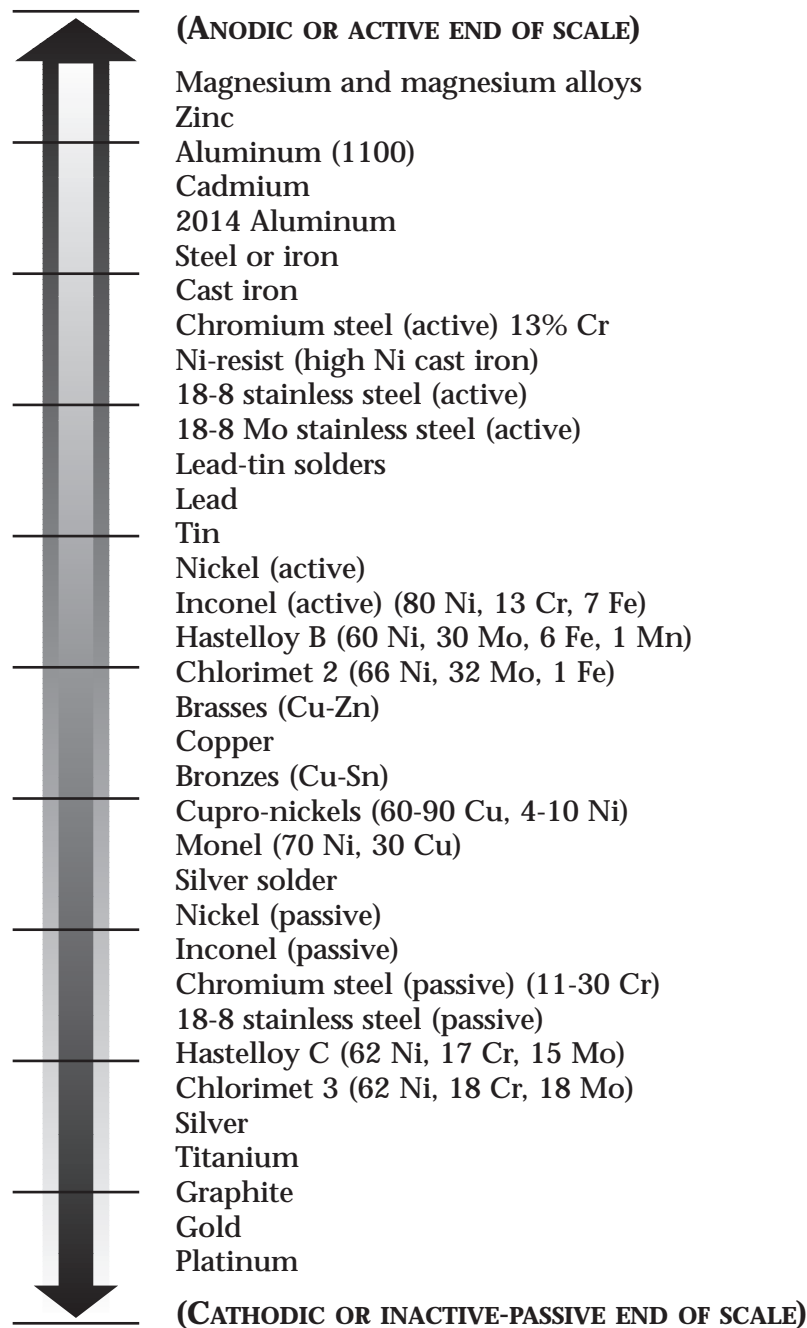
To illustrate the galvanic relationship between dissimilar metals, consider steel and copper. According to the galvanic series, steel is anodic to the copper. If large copper plates were connected together with steel rivets and immersed in seawater (electrolyte), the steel rivets would corrode rapidly and quickly fail. However, if the metals were reversed with copper rivets and large steel plates, the time to failure would be much longer since the area of the anode (steel) to the cathode (copper) governs the corrosion rate. Thus, a large anode and a small cathode is preferred to retard corrosion.

Cavitation. This is a largely mechanical type of corrosion which may be

accelerated by oxygen and which occurs under conditions of high turbulence and velocity. Cavitation takes place when tiny bubbles form on a surface and collapse very rapidly. This action can be destructive to exposed surfaces.

In drilling operations, this type of attack may be found on the outer ends of the “blades” on centrifugal pump impellers. Cavitation is usually more of a problem when the pump suction is restricted.

Galvanic Series, Commercial Metals and Alloys in Seawater



Metallurgy

Metals are crystalline, comprised of a microstructure of grains and grain boundaries. To form a purified metal or alloy, melted liquid metal must be cooled into the solid state. This liquid-to-solid phase change is similar to water freezing into ice. As water cools below 32°F (0°C), ice crystals form. As the temperature continues to cool, the crystals grow until they expand into one another and all the liquid is gone. Metals solidify in a similar way. Solid metal crystals (grains) form and grow until they come into contact with neighboring grains. This contact area between grains is called the *grain boundary*. The metallurgy of the grains is different from the metallurgy of the grain boundaries, and corrosion will affect each differently.

The microstructure and final properties of steel are determined by alloy constituents, temperature, and by the rate and procedure of cooling. Variations in the microstructure determine the properties of steel. Metals are different from other crystalline solids in that they are ductile, allowing plastic deformation without fracturing or permanently

deforming. The point at which a metal permanently deforms and will not return to its original dimensions is called its *elastic limit*. Ductility in a metal is achieved by the grains of the metal being able to slide easily on adjacent grain boundaries (deforming) without failing. Varying the microstructure permits unlimited fabrication possibilities. Metals can be made hard or soft, ductile or brittle, depending on the alloy mixture, the cooling method and rate, and various post-solidification treatments.

Since the most stable configuration of a metal is its particular crystal lattice (shape), grain boundaries represent high energy areas with respect to the grains because they do not align with the crystal orientation. Thus, grain boundaries often are anodic to the grains and are attacked more readily when exposed to a corrosive environment. Tensile strength and hardness are factors in the corrosiveness of oilfield tubular goods. High-strength pipe is harder, less ductile and more susceptible to hydrogen embrittlement, stress corrosion cracking, and/or sulfide stress cracking.

Corrosion Factors

Corrosion is accelerated in acidic environments...

pH. Corrosion is accelerated in acidic environments (pH <7) and retarded in alkaline conditions (pH >7) (see Figure 2). As the pH ($\text{pH} = -\log [\text{H}^+]$) is increased, the concentration of H^+ will be reduced, which may slow the corrosion rate. Conversely, decreasing the pH increases the concentration of H^+ ions, which increases the cathodic reaction and may increase the corrosion rate (acids tend to dissolve metals faster).

High-strength steels are susceptible to hydrogen embrittlement and catastrophic failure in acidic environments. Sulfides do not need to be present for this to occur.

Normally, a pH of 9.5 to 10.5 is adequate to mitigate most corrosion. In some cases, a pH as high as 12 may be required. High pH values (>10.5) neutralize acid gases and lower the solubility of corrosion products.

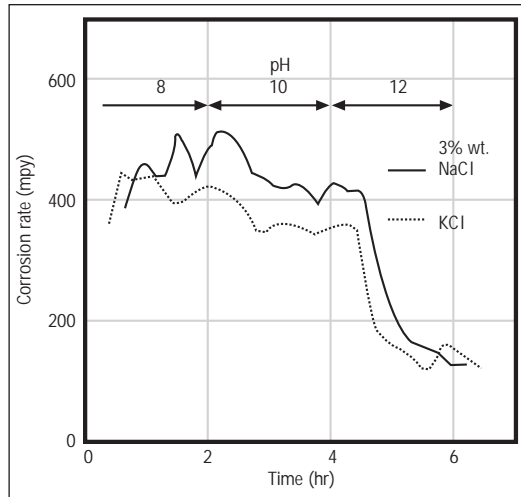


Figure 2: Effect of pH on corrosion.

Aluminum components. High pH is detrimental to aluminum alloys which are subject to extreme corrosion in alkaline environments. Aluminum drill pipe should never be subjected to a pH greater than what is recommended by the manufacturer. If the maximum recommended pH range is not known, the pH should be kept below 9. Never use high-pH mud systems, such as a lime or silicate mud, with aluminum pipe. If aluminum pipe begins turning black, it is probably because alkaline etching is exposing the silicate in the aluminum alloy; lower the pH to 8. Aluminum should not be used in H_2S .

Pressure affects corrosion by increasing the solubility...

Dissolved salts. Salts dissolved in water affect corrosion rates by increasing the conductivity of the water and the potential for high corrosion rates. This contributes to oilfield brines and completion fluids being corrosive.

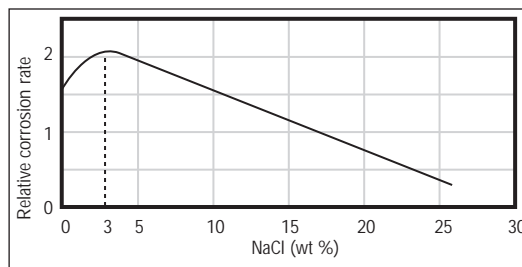


Figure 3: Effect of salinity on corrosion rate.

Although it is not widely known, fluids containing 3% by weight chloride salt can be more corrosive than higher-salinity fluids (see Figure 3). As the salt concentration increases, the dissolved oxygen decreases (see Figure 4). Corrosion rates are higher at approximately 3% NaCl or KCl than at saturation. Seawater and inhibitive potassium (KCl) systems usually have salt concentrations near this level and require corrosion protection.

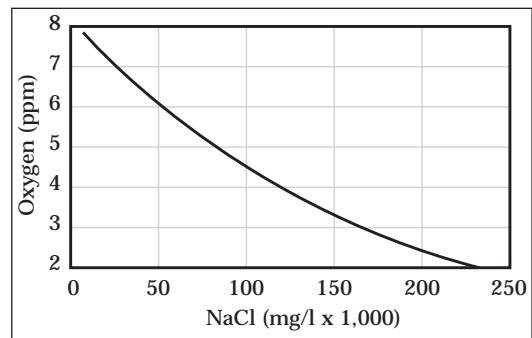


Figure 4: Effect of salinity on oxygen solubility.

The solubility of oxygen in high-salt muds is very low. However, the theoretical oxygen solubility does not limit corrosion in many salt muds. Muds which foam or aerate, i.e., they trap air bubbles, such as non-dispersed salt muds, may have an oxygen content many times the solubility limit.

Pressure. Pressure affects corrosion by increasing the solubility of oxygen and other corrosive gasses (see Figure 5). At 100°F and 100 psi, the solubility of oxygen in freshwater is about 230 ppm

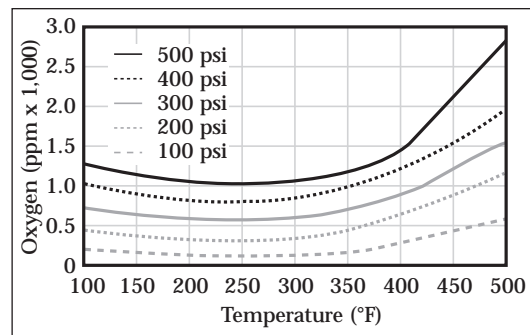


Figure 5: Effect of pressure (and temperature) on oxygen solubility.

Corrosion generally increases with increasing temperature.

(parts per million). At 100°F and 500 psi however, the oxygen solubility increases to 1,270 ppm. It is safe to assume that any oxygen trapped or entrained in water-base mud systems will be completely dissolved at circulating pressures.

Temperature. Temperature has a twofold effect on corrosion. Corrosion generally increases with increasing temperature. The rate of most chemical reactions increases with temperature, and corrosion is simply a chemical reaction.

Oxygen solubility rapidly decreases as temperature increases, at atmospheric pressure. In freshwater, oxygen has a solubility of 14.6 ppm at 32°F and atmospheric pressure. This drops 44%, to about 8 ppm, as the temperature increases to only 85°F and is considered to be zero at the boiling point. As Figure 6 shows, oxygen solubility is quite low at moderate temperatures.

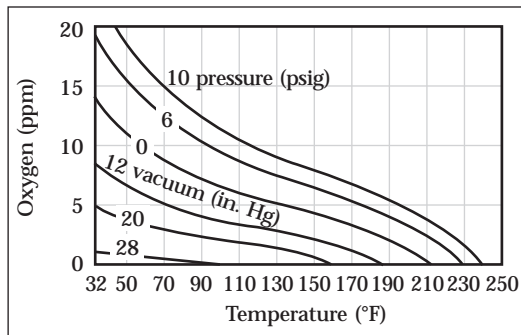


Figure 6: Effect of temperature (and pressure) on oxygen solubility (after Miron).

While higher temperatures may limit oxygen solubility from direct air contact in the surface system, it has little or no effect on the amount of air trapped or entrained in the mud which is circulated downhole.

Figure 7 shows the effect of increased temperature on highly corrosive 3% KCl and NaCl brines. Figure 8 reveals that under dynamic pressurized conditions, increased temperature increases corrosion, that increasing salinity from 3% to saturation decreases corrosion and that removing dissolved oxygen with an oxygen scavenger reduces corrosion even further.

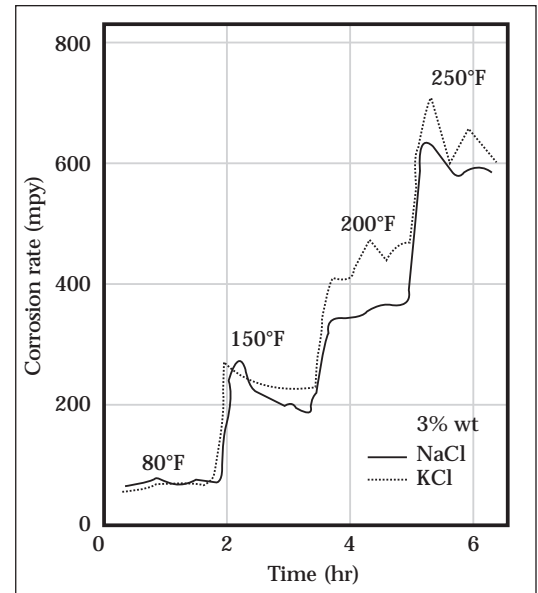


Figure 7: Effect of temperature on corrosion rate for 3% brines.

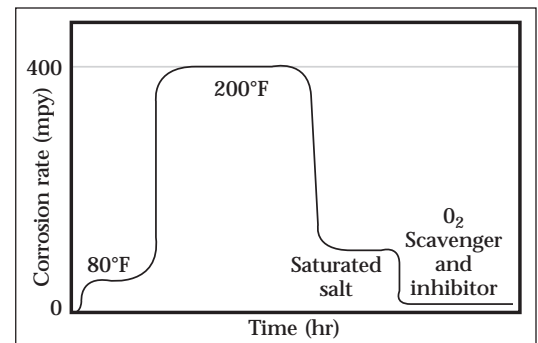


Figure 8: Dynamic corrosion response to temperature, increased salinity and oxygen removal.

Even traces of oxygen can cause pitting...

Scale. Mineral scale is the result of the precipitation and deposition of insoluble compounds, usually calcium, magnesium or barium compounds (CaCO_3 , CaSO_4 , etc.). Soluble metal ions such as Ca^{2+} and CO_3^{2-} can combine to precipitate on downhole tubulars as a CaCO_3 scale. When scale develops on drill pipe, the shielded or isolated area under the scale is vulnerable to pitting attack or may show the “concentration-cell”-type corrosion.

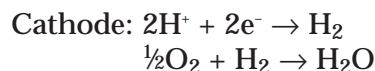
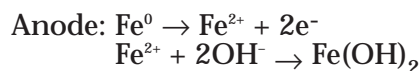
Mill scale is a layer of iron oxides formed during the manufacturing process at the mill. It is electrically conductive and brittle. When new pipe is bent or flexed, the mill scale will crack. Oxygen corrosion will be concentrated and form, as pits, at the base of these cracks. New drill pipe should not be used in corrosive environments without special attention to, and adequate protection from, corrosion. Mill scale will be worn away quickly by handling and contact with the wellbore.

Dissolved gases. Oxygen, carbon dioxide and hydrogen sulfide — are usually the chemical cause of corrosion in drilling fluids. They may be referred to as *corrosive agents*. Corrosion is rarely a problem in drilling fluids unless one or more of these gases is present in solution.

Dissolved oxygen (O_2). This is the leading cause of corrosion in water-base drilling fluids. It is constantly being introduced into the mud system through the shale shaker, mixing hopper, pit stirrers, leaking centrifugal pump packings and hydrocyclones; it is always present in the makeup water. Water-base fluids tend to have high dissolved oxygen under surface system conditions.

Even traces of oxygen can cause pitting and high-corrosion rates. The colder the surface mud temperature, the higher the dissolved oxygen content. Due to air entrapment, the total oxygen content in a mud system can exceed the anticipated oxygen solubility based on temperature, pressure and salinity. Trapped air will quickly be dissolved under pressure, see Figure 5. As this fluid is circulated downhole corrosion rates can significantly increase, resulting in pitting attack.

Reactions that can take place with iron in the presence of oxygen:



A common reaction at the cathode is for hydrogen ions to gain electrons and form atomic hydrogen. If not removed, this hydrogen will “cover,” or polarize, the cathode and slow or stop the corrosion process. When available, oxygen reacts with the hydrogen to remove it from, or depolarize, the cathode. Oxygen enhances the cathodic reaction, which in turn increases the anodic reaction (corrosion rate). Oxygen corrosion often causes, and is characterized by, pitting. Oxygen, a cathodic depolarizer, also increases the severity of corrosion caused by other dissolved gasses, such as H_2S and CO_2 .

Various mud systems contain significantly different levels of dissolved oxygen, and some additives react with this oxygen, reducing its concentration. For example, organic acids such as lignosulfonate, tannin and lignite react rapidly with and reduce dissolved and entrapped oxygen. These chemicals are excellent oxygen scavengers although that is not their primary function.

Carbon dioxide dissolves in water to form carbonic acid...

Deflocculated systems (with low gels) allow entrained air (oxygen) to escape more easily than non-dispersed mud systems.

Polymer systems (such as low-solids, non-dispersed and POLY-PLUS®), seawater systems and salt-saturated systems tend to entrain more air, increasing dissolved oxygen. Many polymer muds also contain low concentrations of salts (e.g. KCl) for hole stability. As discussed earlier, this low level of salt will accelerate corrosion rates which can result in severe attack. CONQOR 404 can be used in these systems to inhibit corrosion, and minimize the effect of dissolved oxygen and corrosive salts.

Carbon dioxide (CO₂). Carbon dioxide dissolves in water to form carbonic acid (H₂CO₃), reducing pH. For this reason, it is often referred to as an “acid gas.” Carbon dioxide will cause corrosion (like other acids) by hydrogen evolution.

Unlike oxygen, carbon dioxide/carbonic acid attacks the iron directly, forming iron carbonate at the anode of the corrosion cell. Hydrogen will polarize the cathode in this process. If oxygen is present, it will depolarize the cathode. With carbonic acid reacting with iron at the anode and oxygen depolarizing the cathode, the combined attack from the two gases will be greater than the sum of the damage caused by each gas acting alone.

The primary treatment for carbon dioxide corrosion is to raise the pH above 6 and/or to precipitate CO₃²⁻ with a source of calcium (such as lime or gypsum). Increasing the pH above 6 will transform the carbonic acid (H₂CO₃) into bicarbonate (HCO₃⁻) at medium pH and carbonate (CO₃²⁻) at higher pH.

Carbon dioxide (acid-gas) attack usually results in pitting and grooving which gives a “worm eaten” appearance. NACE Corrosion Vol. 22, page 244,

1966 documented cracking from CO₂ in a “non-H₂S” environment. The steel tested was an N-80 grade with a Rockwell Hardness (HRc) of 33 to 34. When applicable, small treatments of lime should be used to neutralize the carbonic acid, increasing pH and precipitating calcium carbonate (CaCO₃). The potential for scale increases when using a source of calcium to remove neutralized CO₂, especially at higher pH. A scale inhibitor, such as SI-1000™, should be used to limit the deposition of scale when treating carbon dioxide contamination with calcium compounds.

Monitoring the concentration of CO₂ and related ions with the Garrett Gas Train (GGT) is recommended. When analyzing corrosion coupons, they will effervesce when acidized, if calcium carbonate scale is present.

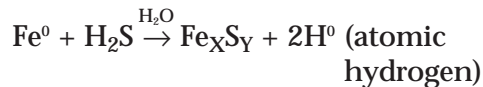
Hydrogen sulfide (H₂S). Is a poisonous gas with a toxicity approximately the same as hydrogen cyanide. It is an extremely dangerous gas with a distinctive, foul, rotten-egg odor which will quickly deaden the sense of smell. *NOTE: H₂S must be handled immediately with the utmost precautions for personal safety and appropriate treatments.* See Hazards and Characteristics of H₂S on page 19.25.

H₂S is a reactive, corrosive, acid gas that can cause serious damage to equipment. The gas can enter a mud system in at least four ways:

1. From drilling H₂S-bearing formations.
2. From being present in makeup water or liquids.
3. From bacterial reduction of sulfates to sulfides in water-base muds.
4. Thermal degradation of mud additives.

The gas dissolves in the water phase to form hydrosulfuric acid. This acid is less corrosive than carbonic acid, but it is very destructive and can cause sulfide stress cracking of susceptible steels.

The simplified chemical reaction of H₂S corrosion can be stated as follows:



Iron sulfide formed by this reaction strongly adheres to steel surfaces as a black scale. Pitting may develop beneath the scale. This pitting may shorten the life of drill pipe by forming the basis for initial cracking and fatigue failure.

Hydrogen ions produced by the above reaction may result in brittle failure of the metal from either stress cracking or hydrogen embrittlement. Hydrogen sulfide is a catalyst or accelerator for the attack of oxygen on steel. Hydrogen ions (protons) released from H₂S or HS⁻ in the sulfide corrosion process are so small that they can easily be absorbed by the steel. These ions can either acquire an electron and become atomic hydrogen or react with carbides in the steel to become acetylene gas. Either gas will become trapped in voids along grain boundaries. As the gas collects, it builds pressure. When this pressure and the load on the pipe exceed the tensile strength of the pipe, it will fail. For high-strength steels like P-110 tubing, concentrations as low as 1 ppm H₂S at low pH will cause cracking over a period of time.

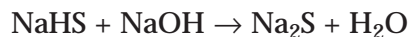
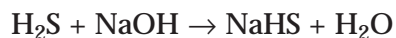
The resistance of steel to brittle failure due to hydrogen sulfide is related to the hardness or yield strength of the steel. High-strength steels are usually more brittle than low-strength steels under normal circumstances. Hydrogen embrittlement is usually not a problem in steels with a Rockwell hardness below 22 or a maximum yield strength below

90,000 psi. High-strength steels with hardness and yield values above these levels should not be used for hydrogen sulfide service. It is recommended that NACE International MR-01-75-document (latest edition) be used as the main guide for selecting metallurgy for use in any H₂S or sour service.

Grade E drill pipe is usually considered safe for use in sulfide service, but work hardening will make it more susceptible to SSC. Pipe which has been stressed near its elastic limit (where it is permanently lengthened by stretching) should not be used in known hydrogen sulfide conditions.

At temperatures above approximately 135°F (57°C) there is evidence that brittle failure is reduced, and it may be possible to use slightly higher grades of casing at the higher temperatures.

Solubility data shows that the solubility of H₂S is about 0.1 molal or 0.2N (3,400 ppm) at room temperature and pressure. When drilling fluids or treating waters are analyzed, somewhat higher figures can be obtained since hydrogen sulfide will react with caustic in the drilling fluids to form alkaline salts, sodium bisulfide, sodium sulfide and water according to the following equations:



Hydrogen sulfide (H₂S) is neutralized into bisulfide (HS⁻) with increasing pH and finally into sulfide (S²⁻). As the pH increases, the percent of total sulfides as hydrogen sulfide decreases to a very low level as shown in Table 1 and Figure 9.

The chemistry of hydrogen sulfide is quite complex.

pH	% S ²⁻ as H ₂ S
5.0	98.000
6.0	90.000
6.5	70.000
7.0	50.000
7.5	25.000
8.0	10.000
9.0	1.000
10.0	0.100
11.0	0.010
12.0	0.001

(% S²⁻ divided by 100 is used in Garrett Gas Train calculation for soluble sulfides.)

Table 1: Effect of pH on hydrogen sulfide.

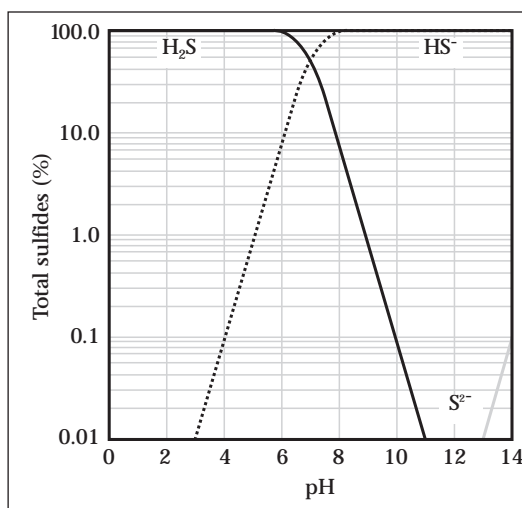


Figure 9: Distribution of sulfides with pH.

Maintaining a high pH is extremely important...

Maintaining a high pH is extremely important in limiting the effects of H₂S problems in drilling fluids because the neutralization reaction is reversible. When H₂S is treated with caustic soda, lime or caustic potash to increase the pH, part of the solubilized acid-gas is converted to soluble sulfides. If the pH is not maintained by continued treatments or if an influx of an acid gas (either more H₂S or some CO₂) is encountered, the pH will decrease. As the pH drops, the soluble sulfides will revert to H₂S.

The chemistry of hydrogen sulfide is quite complex. Sulfides react to form compounds that are entirely unrelated to stoichiometric relations and the simple chemical reactions listed above. The most important consideration is that when H₂S enters an alkaline mud, it reacts to form an alkaline sulfide, most often sodium sulfide. While elevated pH is a good way to keep H₂S from causing problems under certain conditions, it does not remove it from the fluid and any drop in pH can create a significant hazard.

The preferred method for treating hydrogen sulfide or soluble sulfides, is with a zinc-containing product such as SULF-X.[®] This product precipitates sulfide as an insoluble zinc sulfide (ZnS). Under normal conditions and with alkaline pH, this insoluble precipitate will not revert to either hydrosulfuric acid or hydrogen sulfide. Monitor the sulfide level with the GGT and Drager tubes as per API RP-13B-1 and B-2 (latest edition).

CAUTION: Hydrogen sulfide poses significant risks to personnel. See Hazards and Characteristics of H₂S on page 19.25. These risks are increased further by its capacity to cause catastrophic failure of high-strength steels such as casing and drill pipe.

Hydrogen sulfide is a liquid under relatively low pressure and soluble in water-, oil- and synthetic-base muds. During a kick, hydrogen sulfide remains a liquid until it is very close to the surface where it has a phase change to gas with a very rapid and large increase in volume, causing well control, personal safety and corrosion hazards. When hydrogen sulfide comprises a significant percentage of the formation fluid, kick control is especially difficult. Suspected H₂S kicks are often "bull headed" back into the formation to avoid the hazards of circulating an H₂S kick to the surface.

Anyone who anticipates working in an area where exposure to hydrogen sulfide is likely, should assume personal responsibility for becoming familiar with the available safety equipment, safety

procedures, duties and regulations which apply to his or her duties. Precautions and equipment should be used to provide a safe working environment.

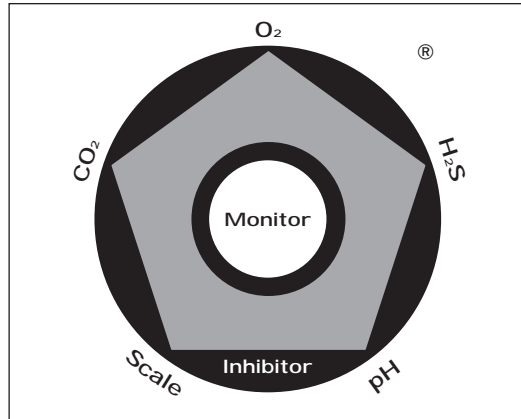
Fluid: Water-base drilling fluids	Contaminant: Oxygen	Source: Atmosphere-entrained by mud guns, shakers, hopper and surface equipment. Absorption
Remedies: (1) Submerge guns and operate mixing equipment only when required. (2) Use degasser. (3) Condition mud to maximize breakout. (4) Add CONQOR 404 inhibitor. (5) Add oxygen scavenger.		
Fluid: Water-base drilling fluids	Contaminant: Carbon dioxide	Source: Gas influx and formation waters
Remedies: (1) Operate degasser. (2) Condition mud properties to maximize breakout. (3) Raise pH to 10 and adjust alkalinity to prevent acid attack. (4) Add CONQOR 202B to pipe. (5) Add calcium source (lime/gypsum) to precipitate the carbonate. (6) Add SI-1000 scale inhibitor to reduce scaling.		
Fluid: Water-base drilling fluids	Contaminant: Hydrogen sulfide	Source: Gas influx, thermal degradation of mud additives and bacterial action
Remedies: (1) Raise the pH to 11.5 or above. (2) Condition mud properties to maximize breakout. (3) Operate degasser with flare. (4) Add SULF-X (zinc oxide) sulfide scavenging agent. (5) Use CONQOR 202B on tube pin and boxes. If using CONQOR 404, increase the concentration. (6) Add oxygen scavenger. (7) Add SI-1000 scale inhibitor. (8) Use non-sulfonate-base additives and pipe dope thread lubricants if at high temperature. (9) Inhibit bacterial growth with X-Cide 207 or glutaraldehyde product. (10) Use inspected tubulars of 90,000 psi yield strength or less with HRC of 22 or less. Use NACE MR-01-75 latest edition. (11) Break over to a high-lime mud or displace with VERSADRIL [®] or NOVADRIL [®] drilling fluid.		
Fluid: Water-base drilling fluid	Contaminant: Bacteria	Source: Makeup water and formation
Remedies: (1) Increase pH to 11.5 or above. (2) Increase salt concentration to saturation if using a salty mud. (3) Inhibit growth with X-Cide 207 or glutaraldehyde product. (4) Add CONQOR 404 to system. (5) Use SI-1000 scale inhibitor. (6) Monitor colonies per ml with serial dilution testing in broth bottles.		

Table 2: Corrosive environments and remedies.

Fluid: Oil- and synthetic-base drilling fluids, packers	Contaminant: Hydrogen sulfide	Source: Formation
Remedies: (1) Raise P_{OM} alkalinity to 2 or above, if not at this level. (2) Tighten emulsion to maximum stability. (3) Pilot test the addition of SULF-X sulfide scavenger.		
Fluid: Air, mist and foam	Contaminant: Oxygen (O_2), carbon dioxide (CO_2) and hydrogen sulfide (H_2S)	Source: Injected air and gas influx into formation
Remedies: (1) Raise pH of injected fluid to 11.5 or above. (2) Add CONQOR 404 inhibitor. (3) Pilot test treatment with makeup water and foaming agents for compatibility.		
Fluid: Geothermal drilling	Contaminant: Temperature, acid gases, erosion and corrosion	Source: Formation and air velocity
Remedy: (1) Add Unisteam™ (Unocal) in recommended concentrations.		
Fluid: Freshwater dispersed XP-20® and SPERSENE™	Application: Packer fluids	Source: Formation and bacterial action
Treatments: (1) Condition mud properties. (2) Raise pH to the maximum acceptable level. (3) Add CONQOR 101 to dispersed mud for packer fluid. (4) Add X-Cide 207 or glutaraldehyde product to aid in sterilizing system. (5) Add oxygen scavenger if desired for further protection. For salt muds use CONQOR 303A for packer fluids.		
Fluid: Clear brine fluids, NaCl, CaCl ₂ and CaBr ₂	Application: Packer fluids	Source: Formation
Treatments: (1) If monovalent, raise pH to 10 with caustic, however, if divalent, do not add caustic because Ca/Mg will precipitate. (2) Add CONQOR 303A inhibitor to clear fluid. (3) Add glutaraldehyde product if tests indicate need for chemical.		
Tubulars: Racked tubulars	Contaminant: Atmospheric exposure	Source: Environment
Remedy: (1) Clean rust and apply filming CONQOR 202B or severe-atmospheric-corrosion inhibitors.		

Table 2: Continued.

Corrosion Control



pH control is one of the most widely used methods for minimizing corrosion.

pH. pH control is one of the most widely used methods for minimizing corrosion. It is economical, versatile, and the solubility and reactivity of various corrosive gases is reduced by raising the pH.

pH values of 8.3 to 9 are usually sufficient to convert carbonic acid

(from CO_2) to its less corrosive state. For hydrosulfuric acid (H_2S), a pH of 12 converts most all hydrogen sulfide into bisulfide and sulfide ions. Maintaining pH values in this range also helps control sulfate reducing bacteria. The pH-related carbon dioxide and hydrogen sulfide relationships are shown in Figures 9 and 10.

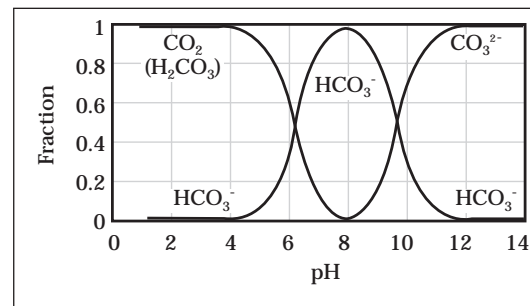


Figure 10: Effect of pH on carbon dioxide.

Corrosion-Control Products

The following products and their methods of application are recommended for use in combating corrosion:

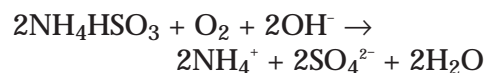
CONQOR 404 can be classified an oxygen inhibitor...

CONQOR 404. This product is an organophosphorus chemical designed to replace the chromate inhibitors. It can be classified an oxygen *inhibitor*, not a scavenger, and works by passivation. It is an all-purpose inhibitor for water-base drilling fluids. It is applicable in freshwater and saltwater fluids and is effective in fluids that are circulated. It is *not* recommended for packer fluids.

The suggested treatment for drilling fluids is 2 to 5 gal CONQOR 404 per 100 bbl of fluid. It is essential to maintain a minimum concentration of the product, and a field test kit is available for monitoring the concentration level. For aerated mud applications, 12 gal/100 bbl is the initial treatment level, but higher concentrations may be required. Usually it is not necessary to add an oxygen scavenger with this particular inhibitor, but it has been done with success. No special pump is needed to add CONQOR 404.

Reduction of oxygen in drilling fluids is an effective method...

Oxygen scavenger. Reduction of oxygen in drilling fluids is an effective method of reducing corrosion. Oxygen scavengers such as ammonium bisulfite and sodium sulfite are used. Ammonium bisulfite is available as an un-catalyzed 45 to 55% active product. The neutralized sulfite anion chemically reacts with dissolved oxygen to form a sulfate anion, thereby reducing dissolved oxygen content. The reaction is as follows:



Freshwater muds generally contain 1 to 5 or more ppm dissolved oxygen, and saturated salt muds generally contain less. The amount of oxygen available for the corrosion process is determined by the total oxygen (dissolved and trapped air) content of the mud and the circulating rate. If the total oxygen content of the mud is 3 ppm, the drill pipe is exposed to twice as much oxygen when the flow rate is 800 gpm as it is when the flow rate is 400 gpm. The oxygen content of a mud can fluctuate significantly when processing equipment is turned on and off. These fluctuations make it impractical to treat stoichiometrically with a scavenger. To assure adequate protection with an oxygen scavenger, sufficient treatments must be added at the pump suction to assure a residual or excess sulfite is returned to the flow line, after it has reacted with all the oxygen being pumped downhole.

The initial required treatment of oxygen scavenger is about 2 gal/hr until 50 to 100 mg/l excess sulfite in the flow line filtrate can be measured. The excess sulfite content can be determined by a titration, e.g. Hach test kit. Upon reaching 50 mg/l excess sulfite, maintain treatment levels as needed to maintain

50 to 100 mg/l excess sulfite in the flow line filtrate. Daily treatments will vary depending on conditions, mud type, temperature, salinity and the flow rate. Typical maintenance treatments are from 24 to 50 gal per day.

Seawater and potassium chloride muds generally require higher sulfite concentrations. As high as 200 to 500 mg/l sulfites may be required. Free calcium removes some sulfite, which of course diminishes the scavenger's effectiveness.

It is recommended that Ca^{2+} concentrations be kept below 200 mg/l. The "makeup" seawater should be treated with 1.5 lb/bbl caustic soda before adding it to the system. This treatment will remove most of the magnesium and calcium to a very low level, by increasing the pH.

The most desirable method of application is by direct addition into the pump suction through a cut-off valve with a chemical injection (proportioning) pump. This kind of metering-device method has been used for many years and has proven to be the preferred method of application, because exposure to air through a mixing hopper would reduce its effectiveness. The chemical pump should always be turned off while tripping. If a proportioning pump is not available, oxygen scavenger solution may be added directly from a drum through a hose extending below the mud's surface. It should always be added as close to the pump suction as possible, not at the shaker. Avoid contact with air because reduction in efficiency will result.

The approximate output of a chemical injection pump in quarts per day can be determined by unscrewing the *pig tail* (bent rod) and allowing the

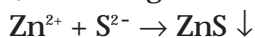
output to flow through the relief port. Collect the pump output for 90 sec. The pump output in quarts per day is approximately the same as the number of cubic centimeters pumped in 90 sec. This procedure is used to set and adjust the treating rate.

For proper utilization of the oxygen scavenger, the entrainment of oxygen should be minimized at the surface by:

1. Running the mixing hopper only when necessary.
2. Avoiding a foamy discharge from the hopper, especially when the discharge is directly in front of the mud pump suction.
3. Proper use of defoamers when needed.
4. Maintaining a full level of mud in the suction pit. This helps avoid vortexing from the mixers and minimizes the foam generated from the hopper and solids-control equipment discharges.
5. Replacing leaking centrifugal pump packing.

SULF-X H₂S scavenger. This is a specially ground, high-surface-area zinc oxide compound for use as a hydrogen sulfide scavenger in drilling fluids. SULF-X should be pilot tested before it is added to oil- or synthetic-base muds because it may increase the need for emulsifiers and wetting agents. Hydrogen sulfide gas that dissolves in the water phase of a mud, is a primary cause of SSC and hydrogen embrittlement in susceptible steels.

SULF-X scavenges sulfides to form zinc sulfide, an insoluble product at a pH of approximately 3 or higher. This ensures a permanent removal. The only exception would be an extremely unlikely event where the pH of the mud dropped below 3 (*i.e.*, during acidizing).



With the acid gas neutralized and precipitated, there is less danger of sulfide

corrosion. Recommended pretreatment levels are from 1 to 2 lb/bbl. Subsequent treatment should start at 1 lb/bbl per 1,100 mg/l sulfides. Actual removal rates may be lower, depending on the mud chemistry. SULF-X appears to be stable to 400°F and is not normally affected by the salinity of the system.

The zinc compounds such as SULF-X may cause flocculation and increased viscosity; zinc is more soluble at pH levels above 11.5, possibly causing flocculation. This is a particular concern in non-dispersed muds. Pilot tests should be made to avoid problems in all cases. Non-dispersed muds which will not satisfactorily tolerate a pH of 10.5 or greater should be dispersed prior to drilling known hydrogen sulfide zones.

Because of its fine grind, SULF-X may increase the viscosity of muds that have high concentrations of low-gravity solids. If a centrifuge is used on a mud containing SULF-X, it will discard the SULF-X. Additions of SULF-X will be needed to compensate for this.

Zinc may be toxic in certain environmental bioassay tests. This should be evaluated prior to using zinc containing scavengers.

SI-1000 scale inhibitor. Scale inhibitors are used to limit the precipitation and deposition of mineral scales on metal surfaces. SI-1000 is an organic phosphate scale inhibitor which has proved effective in reducing scale problems in drilling applications. Initial treatment in drilling mud is 1 gal per 200 bbl mud. Maintenance treatments of 5 gal per tour are usually adequate to control scale.

Bactericides. The reduction of sulfates to sulfides by the bacteria *Desulfovibrio desulfuricans* can occur in drilling fluids, and particularly in storage muds and packer fluids, resulting in a source of hydrogen sulfide. These bacteria are active in low-oxygen environments such as poorly aerated fresh makeup water, brackish water or sea waters in

Scale inhibitors are used to limit the precipitation and deposition of mineral scales...

Glutaraldehyde controls bacteria in all water-base drilling...

the pH range of 5.5 to 8.5. Since the potential for damage from sulfate-reducing bacteria is greatest in packer fluids or storage muds, a microbiocide is strongly recommended for controlling these bacteria.

Glutaraldehyde (25% active liquid) controls bacteria in all water-base drilling, completion and packer fluids. It is effective against aerobic as well as anaerobic bacteria, and a higher concentration can be used if needed. All biocides should be end-use registered with the EPA (or appropriate local regulatory agencies) for oilfield use, such as X-Cide 102, Green-Cide 25G and others. Initial treatments for a 25% glutaraldehyde range from 0.4 to 8.0 gal/100 bbl (100 to 2000 ppm).

If an isothiazolin-type biocide (X-Cide 207) is used to prevent starch fermentation and control bacteria, the initial treatment should be $\frac{1}{2}$ to $1\frac{1}{2}$, 6 lb-jugs per 100 bbl. Maintenance treatments are $\frac{1}{4}$ jug per 100 bbl per day. These products have the active chemical absorbed into an inert insoluble carrier. The product can be added directly to the suction pit at a rate of 5 min per jug. The total initial treatment should be evenly spaced over one circulation. Makeup water should also be pretreated. For severe conditions, add 3 jugs per 100 bbl fluid, and use daily treatments of $1\frac{1}{2}$ jugs per 100 bbl. (This product is not normally added to clear, solids-free brines due to the inert carrier being insoluble.) Packer fluids should be treated with 2 jugs per 100 bbl fluid (0.12 lb/bbl).

Treatment effectiveness and bacteria population can be estimated by using a serial dilution technique with broth

bottles. Observe caution when handling all biocides. Read and adhere to the warning labels on the registered chemical containers.

Amines. Filming amines are effective corrosion inhibitors in drilling fluid environments. They have the ability to displace water in pits and fatigue cracks on the metal surface. Their chemical structure allow them to physically adsorb on steel surfaces, forming a protective oil-wet film. They are most effective when applied directly to drill pipe, but are also effective when applied in batch or uniform treatment. The pipe should be kept clean of scale and coated. The organic film tends to "water-proof" the steel. There will be occasions when a hydro-blast (high-pressure water blast) may be needed to remove rust and scale before application. Amines cannot provide protection beneath scales and pipe rubbers. If concentration cells beneath the ends of pipe rubbers are a problem, the system should be treated continuously with oxygen scavengers.

CONQOR 101. This product is an oil soluble, water dispersible amine inhibitor designed primarily for freshwater-base XP-20/SPERSENE packer fluids. It is recommended for freshwater, dispersed fluids. The recommended treatment is $\frac{1}{2}$ gal CONQOR 101 per barrel of packer fluid.

CONQOR 202B. An oil-soluble filming corrosion inhibitor for direct application and batch treatment of drill pipe. Batch (slug) treatments are made by pumping 5 gal or more of a slug down the drill pipe to coat/film the steel surfaces. Up to 25-gal batches can be used according to the severity of

the corrosion problem. It can be diluted at a 1:5 ratio with diesel or low-toxicity oil if this is allowed. Diluted treatments are not as effective as full-strength treatments, but can be used if desired. Batch treatments of 15 to 25 gal have been effective for 10,000 ft of drill pipe. After the initial treatment, 5-gal slugs can be pumped on connections to maintain the protective film.

CONQOR 303A. This product is a water/brine-soluble amine. It is designed primarily for NaCl, KCl, CaCl₂, and CaBr₂ brines and completion fluids. The recommended treatment is one drum CONQOR 303A per 100 bbl fluid (approximately ½ gal/bbl). It can be added directly to the fluid. The chemical is not effective in, or recommended for, heavy-zinc-containing brines.

Additive	Application	Treatment
CONQOR 101 (adsorption)	Freshwater XP-20 and SPERSENE packer fluid	½ gal/bbl
CONQOR 202B (adsorption)	Freshwater or saltwater drilling fluids	<ul style="list-style-type: none"> • Spray or wipe on pipe • Slug - pour down pipe on connections
CONQOR 303A (adsorption)	Clear brines; NaCl, KCl, CaCl ₂ and CaBr	½ gal/bbl
CONQOR 404 (passivating inhibitor)	All water-base drilling fluids	0.25 to 1 lb/bbl
55% Ammonium bisulfite (oxygen scavenger)	Fresh or salty water-base drilling fluids	Approximately 1½ gal/hr injected to a residual of 300 to 500 mg/l SO ₃ ²⁻
X-Cide 207 (bactericide)	Water-base drilling, completion and workover fluids	½ to 1½ jugs/100 bbl; 3 jugs maximum per 100 bbl
25% glutaraldehyde (bactericide) X-Cide 102 or Greencide 25G	Water-base drilling, completion and workover fluids	100 to 2,000 ppm – 0.4 to 8.0 gal/100 bbl
SULF-X (sulfide scavenger)	Water-, oil- and synthetic-base fluids	Zinc oxide product to treat sulfides. Treats out sulfides at 1,100 mg/l sulfides per lb/bbl. Concentration 1 to 2 lb/bbl. Monitor for sulfides with GGT and treat accordingly. For oil and synthetic muds, pilot test for effect on system.
SI-1000 (scale inhibitor)	Fresh or sodium-chloride-base drilling or completion fluids	Add 5 to 10 gal of product diluted with freshwater per tour. Desire 5 to 10 mg/l organic phosphate in filtrate.

Table 3: M-I corrosion-control additives.

Monitoring corrosion is performed with corrosion coupons...

All corrosion coupons should be machined to fit...

Corrosion Measurements

Corrosion ring coupons. Monitoring corrosion is performed with corrosion coupons inserted in the last drill pipe box before the heavyweight drill pipe or collars and in the kelly saver sub. These pre-weighed “rings” of steel should be left in the drill pipe for an exposure period of approximately 100 hr. The test procedure for evaluating these coupons is described in API Bulletin RP-13 B-1. This evaluation will tell not only the rate at which corrosion is occurring, but also the type of corrosion (i.e. oxygen-, carbonate- or sulfide-caused corrosion).

Removal and examination of these rings, after a period of exposure, is essential to applying the proper remedial corrosion-control program. This analysis will indicate the corrosiveness of the drilling fluid and the type of corrosion encountered. An examination of any scale deposits and pits on the rings gives clues as to the cause of the corrosion, thus aiding in choosing proper remedial action. For example, if iron oxide is present, then dissolved oxygen is suspected. If iron sulfide is present, hydrogen sulfide is suspected, and if iron carbonate or calcium/magnesium carbonate is present, carbon dioxide is indicated.

A common corrosion byproduct of oxygen corrosion is magnetite (Fe_3O_4). It can be identified by its magnetic property and its acid insolubility. Various other oxides of iron, such as $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are also common. Oxygen-corrosion deposits are identified by their dark rust-brown to black color and moderate solubility in inhibited 15% HCl. The oxide deposits do not dissolve immediately in the acid used to clean the rings prior to weighing and usually require several dips in the acid or wiping with steel wool or wire brush.

Iron carbonate (FeCO_3), or siderite, is the common byproduct of CO_2 corrosion. It can be determined by its characteristic slow effervescence (bubbling) in 15% HCl or with the FeS test solution (acid arsenite test solution). The bubbling gas is actually the escape of carbon dioxide gas from the scale. Calcium carbonate scale will cause more rapid effervescence (fizzing).

Iron sulfide scale (FeS) will form on the drill pipe when corrosion by sulfides occurs. Iron sulfides are black. Iron sulfide scale is identified with the iron sulfide (acid arsenite) test solution by a bright yellow precipitate. The yellow precipitate forms when the acid arsenite solution comes in contact with the sulfide scale. The precipitate resembles “miniature scrambled eggs” and has some shape and substance, not just the yellow color. Iron sulfides preferentially oil-wet. If the mud contains oil, this test may be slow or not work until the pipe is washed or degreased with an alkaline soap.

The corrosion coupon is not capable of providing information relating to hydrogen embrittlement, stress corrosion cracking or other forms of fracture, except in the manner in which pitting may relate to these failures.

All corrosion coupons should be machined to fit in the relief groove of the tool joint box for a proper fit. They should have the same bore as the drill pipe to minimize turbulence. Corrosion rings are normally cut from tubes that have not been quenched and tempered. The similarity in metallurgical composition to drill pipe should be adequate to minimize galvanic effects and provide useful data.

Pitting generally occurs in salt solutions...

Drill pipe corrosion coupons should be kept in the drillstring for a minimum of 40 hr, with 100 hr being the desired period of exposure. Coupons can be left in the drillstring for more than one bit run.

Care should be taken to ensure that the box recess is clean to avoid ring damage. This prevents interference with proper makeup of the joint and avoids ring damage. During installation, the ring should be handled only with clean, dry gloves.

The drill pipe corrosion ring form should be filled out completely. Each form should have a space for ring material, drilling fluid properties, type of corrosion, location of ring in drillstring, initial weight, time, depth in, depth out, ring number, color of scale and any other significant information for the specific test. The form may be printed on a mailing envelope for the ring or on a separate form to be enclosed with the ring.

Drilling fluid residue should be removed from the corrosion ring by wiping with a cloth when it is pulled from the drillstring. The ring should be examined for severity of corrosion or mechanical damage. If severe corrosion is evident, the cause of the corrosion should be determined promptly so remedial action can be taken.

Following visual examination, *wipe and dry the coupon*, then place it in the vapor-inhibited paper to further retard corrosion. **Do not coat with pipe dope or oil.** Place the coupon into the mailing envelope.

The evaluation of rings is important in the field as well as in the laboratory. The visual inspection upon removal is often the best. If obvious corrosion is evident, it is normally observed as pitting corrosion. It is important to note

how extensive the pits are. Pitting generally occurs in salt solutions because of the increased conductivity of the fluid, along with dissolved oxygen. Pitting also is characteristic of certain materials that form oxide films or coatings. Uniform attack or general corrosion can best be determined by weight-loss measurements with the coupons.

The corrosion ring envelope should be stamped with the initial weight of the ring and a "K" factor. The K factor is used to convert the weight loss per time into weight loss per surface area of the ring and time. It is a straight mathematical conversion from grams to pounds and for the surface area of the coupon. The corrosion rate of the ring is calculated with K by the following formula:

$$\text{Corrosion rate (lb/ft}^2\text{/yr)} = \frac{K \times [\text{initial wt (g)} - \text{final wt (g)}]}{\text{total exposure time (hr)}}$$

$$\text{Corrosion rate, mils/yr} = \text{corrosion rate, lb/ft}^2\text{/yr} \times 24.6$$

Corrosion rings should be inspected for physical or mechanical damage. Mechanical damage to the ring will often be indicated by cuts, gouging or dents to the outer surface of the ring. If mechanical damage results in the loss of metal, it will negate the corrosion rate calculation. If there is any evidence of damage, it should be reported and the corrosion rate should not be calculated or reported. However, any description of corrosion, such as pitting and positive sulfide or carbonate deposits, etc., should still be reported.

Corrosion rings are machined to fit in specific drill pipe tool joints. Be sure to specify the drill pipe tool joint size and type when ordering corrosion rings (see Table 4).

Tool Joint Size (in.) and Type	Fann Ring Number	OFI Ring Number	K-Factor (lb/ft ² /yr)
2 ⁷ / ₈ IF, 3 ¹ / ₂ SH	63618	18014	394
3 ¹ / ₂ XH, 3 ¹ / ₂ FH	63619	18016	357
3 ¹ / ₂ IF, 3 ¹ / ₂ XH	63620	18018	337
4 FH	63621	18020	256
4 IF, 4 ¹ / ₂ XH	63623	18022	250
4 ¹ / ₂ FH, 4 ¹ / ₂ XH, 4 IF	63624	18024	207
4 ¹ / ₂ IF, 5 XH	63625	18026	253
5 ⁹ / ₁₆ , 5 ¹ / ₂ API Reg. FH, 6 ⁵ / ₈ API Reg.	63626	18028	134
6 ⁵ / ₈ FH	63627	—	202
4 ¹ / ₂ XH	63629	18030	184
5 XH	63631	18032	210/179

Table 4: Corrosion ring coupon numbers and K-factors.

The probe is installed in the mud circulating system...

Probes. Galvanic probes have been used in aqueous systems in the petroleum industry for a number of years. They can help indicate the corrosiveness of a fluid by generating a current which is measured by a recorder. Galvanic probes have been found to be useful in monitoring oxygen entry in water floods also. Most drilling fluids are extremely corrosive when oxygen is present. These probes cannot be expected to be a quantitative tool in the drilling fluid because of the constantly changing aqueous media. The probe is installed in the mud circulating system, usually in the standpipe. When placed in the standpipe, these probes reflect the effects of the mud's trapped or entrained oxygen as well as the dissolved oxygen due to the pressure in the standpipe.

As the name implies, the galvanic probe is a bimetallic couple (usually brass and steel) constructed so that the current output can be measured on a modified recorder for a continuous record of events. When placed in a water system, the current output will

stabilize at some value that reflects the conditions in the system. Any change in the system that will change the current output will be reflected on the recorder.

While the probe is affected by many things, such as flow rate, temperature and inhibitor films, it is extremely sensitive to dissolved oxygen. In most oxygen-free systems, the probe will polarize and the output will approach zero. Even small quantities of oxygen will depolarize the probe and the current output will be increased.

The galvanic probe can be a valuable asset to routine monitoring and for troubleshooting problems. The galvanic probe is a rugged line instrument that requires a minimum of care. With the proper recorder, it provides a record the driller can watch from the rig floor. It will indicate air leaks and malfunctions in the system so that corrective measures may be taken before severe damage occurs. This aids in creating an important awareness of corrosion problems.

Correlation of the galvanic probe measurements with the drill pipe coupon corrosion rate will not be exact, for several reasons. For example, the steel anode element may become severely pitted, and calcium carbonate scale deposition can also influence the

probe reading. If signs of scale are present, the probe elements should be cleaned periodically. Likewise, if the mud system is in a sour environment (H_2S), the probe elements may oxidize, turning brown or black and result in a false reading.

Packer Fluids

Water-base packer fluids should be conditioned for long-term stability and to minimize corrosion. It is important to increase the pH to some optimum level, utilize an appropriate biocide and possibly a dispersible filming inhibitor. The high pH helps in reducing the corrosion rate, the biocide should prevent sulfate reducing bacteria activity and a filming inhibitor will coat the steel surfaces. The filming inhibitor should aid with a film on the pipe to “insulate” it from the corrosive aqueous environment.

The oil- or synthetic-base muds used as packer fluids should also be conditioned for optimum long-term stability and the emulsion tightened to help control corrosion. The mud alkalinity, P_{OM} should be raised to keep the internal phase highly alkaline. Normally these muds do not have inhibitors added to them because their oil-wetting nature aids in reducing corrosion of the steel tubulars, and they usually have lower corrosion rates better than water-base packer fluids.

The high pH helps in reducing the corrosion rate...

Hazards and Characteristics of H₂S

Hydrogen sulfide gas has an offensive, rotten-egg odor at low concentrations and cannot be smelled at higher concentrations. This colorless, highly reactive acidic gas is hazardous to workers and detrimental to drilling equipment, even at low concentrations. H₂S is heavier than air and when released will accumulate in low-lying areas. Closed compartments and storage tanks are particular hazards. H₂S can even accumulate in the top portion of mud pits when there is little wind or air movement. Lethal concentrations can accumulate above mud pits or in tanks even when the concentration of H₂S is so low that it might be considered trivial. Whenever H₂S is present or thought to be a possibility, all rig personnel should be warned not to bend over, or reach down into, the mud pits. The gas is highly flammable and forms an explosive mixture with air.

Even short periods of exposure to hydrogen sulfide can kill or seriously injure humans and can cause catastrophic failure of steel tubulars. The American Petroleum Institute's "Recommended Practices for Safe Drilling of Wells Containing Hydrogen Sulfide" (API RP49) covers in detail both the hazards and safe practices for drilling operations in H₂S zones.

The maximum safe level for repeated worker exposure, the threshold limit, is only 10 ppm H₂S. The accepted industry standard is to wear respiratory protection for concentrations greater than

10 ppm. The hazardous limit, or the concentration that may cause death, is 250 ppm/hr. Unconsciousness occurs after short-term exposure to a concentration of 500 ppm, then breathing stops and death occurs if the condition is not quickly treated.

The following are the physical effects of exposure to hydrogen sulfide:

- 10 ppm — Obvious and unpleasant odor; repeated exposure without adverse effects.
- 15 ppm — Short-term exposure limit (15 min).
- 20 ppm — Burning eyes and irritation of respiratory tract (1 hr).
- 50 ppm — Loss of sense of smell (15 min); headache, dizziness and staggering (1 hr).
- 100 ppm — Coughing, eye irritation and loss of sense of smell (3 to 15 min); altered respiration, eye pain and drowsiness (15 to 20 min); throat irritation (1 hr).
- 200 ppm — Sense of smell impaired rapidly, eyes and throat burn.
- 500 ppm — Unconsciousness occurs after short exposure and breathing stops, if not treated quickly; dizziness, loss of sense of reason and balance; victims need prompt artificial ventilation cardiopulmonary resuscitation.
- 700 ppm — Unconsciousness occurs quickly; death results if the victim is not rescued and treated promptly.
- 1,000 ppm — Unconsciousness occurs immediately followed by death within minutes.