CORROSION IN DRILLING OPERATIONS, CAUSES AND TREATMENTS

By Michael Benning

It is estimated that corrosion accounts for material losses in the range of 8 to 10 billion dollars per year. In this reference we are speaking of corrosion of plastics, fabrics and many other materials in addition to the more familiar corrosion of metals. Corrosion in this respect is the deterioration of materials over time when exposed to the elements of nature.

In this discussion however, we will be dealing with corrosion as it effects the drilling industry and more specifically downhole corrosion while drilling. We will be concerned primarily with corrosion of ferrous metals in an aqueous environment. A definition of such corrosion is 'the tendency of a refined metal to return to its natural composition'. When a metal is refined energy is consumed, the natural tendency of the metal is to return to the state of lower energy, usually some form of metalic oxide.

There are two basic categories of corrosion which can occur, wet and dry. Dry corrosion is usually associated with the interaction of metals with super heated gasses, consequently we will only be concerned with the aspects of wet corrosion.

WET CORROSION

Wet Corrosion is routinely divided into eight different categories, these are:

Galvanic Corrosion

Results from two dissimilar metals connected and immersed in an electrolyte. An automobile battery works on this principle.

Uniform Corrosion

Results when the entire exposed surface corrodes uniformly. This is usually the least damaging form of corrosion.

Pitting Corrosion

Localized corrosion resulting in pits or crevices. Pitting frequently leads to washouts in drill string.

Concentration Cell Corrosion

Also called shielding. This is another type of localized corrosion due to a difference in oxygen concentration.

Intergranular Corrosion

Corrosion may occur in the boundaries between different metals in an alloy due to different characteristics of the metals.

Stress Corrosion

Refers to any type of corrosion accelerated by stress.

De-Zincification

A type of corrosion that occurs in some alloys. It refers to the leaching out of certain components in the alloy.

Erosion Corrosion

Corrosion coupled with erosion due to a moving gas or liquid. This will be accelerated if there are particles suspended in the liquid.

MECHANISM OF CORROSION

In this discussion we are concerned with the corrosion of iron in an electrolyte, the iron represented by the tubular goods and the electrolyte by the drilling fluid. The speed at which corrosion will take place is determined by the conductivity of the fluid in question. Generally, the higher the electrical conductivity the higher the rate of corrosion.

The electrochemical process of corrosion is usually broken into two distinct sets of equations. Those that occur at the anode (anodic) and those that occur at the cathode (cathodic).

Anode

The anode is the site of metal loss. It is characterized by positively charged metalic ions going into solution. The charges on the ions result from the loss of one or more negatively charged electrons. The anodic reaction in the corrosion of drill pipe is represented by the following equation:

$$Fe \rightarrow Fe^{+2} + 2e^-$$

Cathode

The reactions at the cathode will vary depending upon the constituents in the aqueous solution involved. The cathode is usually added to, coated, or protected during the electrochemical reaction. Some examples of cathodic reactions are as follows:

Hydrogen evolution in acid solutions:

$$2H^+ + 2e^- \rightarrow 2H^\circ \rightarrow H_2\uparrow$$

Oxygen reduction in acid solutions:

$$O_2 + 4H^+ + 3e^- \rightarrow 2H_2O$$

Oxygen reduction in neutral or alkaline solutions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The process at the cathode involves the neutralization of the electrons liberated by the anodic reaction. This may involve liberation of hydrogen gas, formation of water or, in the case of a galvanic cell involving two dissimilar metals, the coating of the cathode by metal ions from the anode. Since drilling fluids are generally run in the alkaline range and usually contain some oxygen, the last two reactions will be more prevalent.

The cathode and anode as we relate them to downhole conditions are not large distinct areas, but rather are microscopic areas usually immediately adjacent to each other. The current necessary for the formation of the corrosion cell is generated by microscopic differences in the granular structure of the steel or small localized variations in electrolyte concentrations. The location of the anodes and cathodes are generally not restricted and consequently will vary frequently during exposure. It is this rapid change of locations of the electrodes which leads to a uniform type of corrosion. In the event the anode and cathode do not change location, the effects of corrosion will be more localized and tend to result in pitting or crevaces.

Requirements for Corrosion

There are three basic requirements for corrosion to occur: a corrodible metal, an electrolyte and some acidic substance.

The corrodible metal, under downhole conditions, will be the tubular goods. The electrolyte is an aqueous drilling fluid which may include mist and foam. The most common acidic substances are oxygen (O_2), hydrogen sulfide (H_2S) and carbon dioxide (CO_2).

OXYGEN CORROSION

Oxygen corrosion is certainly the most common source of corrosion in the oilfield. Drilling fluids exposed to the atmosphere will absorb a certain amount of oxygen. This effect is compounded by hoppers left running and mud guns discharging above the surface of the mud as well as centrifugal pumps which suck air through glands or packings. One of the simplest and least expensive means of reducing oxygen entrappment into a mud system is awareness and alleviation of these potential problems.

The mechanisms of oxygen corrosion are not fully understood however some basics are known, the chemical reaction is as follows:

$$2Fe + 3O + H_2O \rightarrow \underset{\text{Ferrous Oxide}}{2FeO(OH)} \rightarrow \underset{\text{Ferric Oxide}}{Fe_2O_3} + H_2O$$

The Ferrous Oxide and Ferric Oxide are the commonly known rust products seen on steel. Several factors influence the severity of an oxygen corrosion problem. Oxygen solubility in an aqueous fluid tends to increase with decreasing temperature and decrease with increasing salinity (See Fig. 1). Consequently, corrosion rates are often increased in the winter months and decreased in highly saline drilling fluids. pH is also known to have some influence on corrosion rates, generally higher pH will mean reduced corrosion. It must be understood however, that high pH will not eliminate corrosion and often is not effective in reducing a corrosion problem.

Frequently it is necessary to use additional corrosion control products to combat oxygen corrosion. This is even more true today as we seem to be seeing an increase in some areas in the use of non-dispersed polymer muds as opposed to the highly treated lignite/lignosulfonate muds. These muds are more prone to entrap and entrain atmospheric oxygen due to their generally higher gel strengths. The lignosulfonates and lignins used in the highly treated muds are also good oxygen scavengers and average higher pH values both of which help reduce the effects of oxygen in the mud.

A number of oxygen scavengers are available on the market. Sodium sulfite ($NaSO_3$), a powdered material and ammonium bisulfite in liquid form are two of the most common. A simplified equation for the reaction of oxygen and sodium sulfite is as follows:

$$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$$

These materials are metered into the suction line at a rate to maintain 100 to 300 ppm sulfites at the flowline. The concentration of sulfites is easily determined by titration of a filtrate sample.

The sulfite type oxygen scavengers are less effective in high hardness brines and injection rates should be increased accordingly. Sulfites are also incompatible with aldehydes used as biocides in drilling fluids. In these cases it may be advantageous to use a passive type of corrosion inhibitor. A passive corrosion inhibitor is one which forms a protective coating on the exposed metal surfaces.

The most common form of passive inhibitor is a chromate. Sodium and zinc chromates are the most prevalent. The chromate groups aid in forming a passive chromic and ferric oxide film at the anodic sites inhibiting further corrosion action at that location. In addition, the zinc chromates will form a zinc hydroxide film on the cathodic sites. These films are easily eroded and must be continually replenished. To this end a relatively high concentration of chromates must be maintained in the drilling fluid, 200 to 500 mg/l in freshwater and up to 1,200 to 1,800 mg/l in saturated brines. The concentration of chromates is easily determined through a simple titration of a filtrate sample.

There are also some amine type inhibitors used in special situations. The amine type inhibitors form a more durable film than the chromates and are more often applied using a spray applicator. Periodic slug maintenance treatments are poured down the drill pipe during connections. The amine inhibitors are varied in formulation to make them suitable for use in water-base fluids, air drilling or heavy workover brines.

CARBON DIOXIDE

The most common source of carbon dioxide (CO_2) is from the formation although occasionally degradation of mud treatment chemicals will cause the formation of CO_2. CO_2 when it solubilizes forms carbonic acid as shown:

CO_2	+	H_2O	→	H_2CO_3
Carbon Dioxide		Water		Carbonic Acid

This immediately reduces the pH of the fluid which increases the corrosiveness of the fluid. In addition, the carbonic acid can react with iron to form an iron carbonate scale on the drill pipe. The scale formation can lead further to a tendency to pitting and severe localized corrosion.

Fe	+	H_2CO_3	→	$FeCO_3$	+	H_2
Iron		Carbonic Acid		Iron Carbonate		Hydrogen

The presence of even very small amounts of oxygen along with a CO_2 influx can result in very severe corrosion due to the strong oxidizing ability of oxygen.

Treatment for CO_2 contamination consists mainly of increasing the pH with caustic and additions of lime or gypsum to precipitate the CO_2 as calcium carbonate ($CaCO_3$). It may also be necessary to use an oxygen scavenger to lessen the overall corrosion rate and a scale inhibitor to prevent the $CaCO_3$ from being precipitated on the drill pipe as scale.

HYDROGEN SULFIDE (H_2S)

Hydrogen sulfide contamination in a drilling fluid comes primarily from the formation although there are some bacteria which will also produce H_2S. The most important aspect of H_2S is that it is extremely toxic to human and animal life. H_2S can be fatal in a matter of minutes at relatively low concentrations. (See Table 2)

H_2S is an acid gas and like CO_2 will lower the pH of a drilling fluid making it generally more corrosive. In addition, presence of any oxygen will increase the severity of the corrosive action. There are a number of chemical reactions associated with the influx of H_2S into an alkaline aqueous fluid.

H_2S may react with the iron to form an iron sulfide scale. This scale may increase corrosion in the area by producing a corroion cell due to differences in electrolyte concentration caused by the presence of the scale.

Another aspect of H_2S contamination is referred to as sulfide stress cracking or hydrogen embrittlement. The hydrogen radicals liberated by the reaction of H_2S with the steel can penetrate and migrate through the crystal lattice of the steel. If the concentration ofthese radicals is high enough cracking of the steel can occur. As a generalization steel with a yield strength less than 100,000 psi is not susceptible to sulfide stress cracking.

H_2S is quite soluble in aqueous fluids and will ionize in two main stages in an alkaline fluid.

H_2S	+	$NaOH$	$\rightleftharpoons$	Na^+	+	HS^-	+	H_2O
Hydrogen Sulfide		Sodium Hydroxide		Sodium Hydrosulfide				Water

$NaHS$	+	$NaOH$	$\rightleftharpoons$	$2Na^+$	+	$S^=$	+	H_2O
Sodium Hydrosulfide		Sodium Hydroxide		Sodium		Sulfide		Water

These reactions are easily reversed by decreasing the pH of the solution. One of the first defenses against effects of H_2S is the alkalinity of the mud which leads to the disassociation of the H_2S to its relatively harmless forms. This is misleading however, because any reduction of pH such as that associated with further influx of the gas can cause a reversal of the above equations and a reformation of the H_2S held in the system. For this reason it is essential to precipitate the H_2S as an insoluble salt. The most common chemicals used to this end are zinc based such as zinc carbonate. The reactions involved are:

$ZnCO_3$	+	H_2S	$\rightarrow$	CO_3	+	ZnS
Zinc Carbonates		Hydrogen Sulfide				Zinc Sulfide (insoluble)

Ironite sponge, a ground iron mineral, is also used as a sulfide scavenger and works under a similar principle. The ironite sponge tends to work better as a system preventative rather than a post contamination treatment.

Sulfide contamination from bacterial action results mainly from contamination by bacteria of the genus desulfovibrio. These bacteria reduce inorganic sulfates ($SO_4^=$) to sufides. This is an anaerobic reaction and is generally restricted to stagnant areas in a well. Treatment for bacterial sulfides is the same as above, but a biocide should also be used to eliminate the bacterial contamination.

ALUMINUM DRILL PIPE

While aluminum drill pipe is not frequently encountered in the oilfield, it is seen occasionally and should be considered in this discussion. Aluminum, in many ways, is considerably more resistant to corrosion than steel. A naturally occurring oxide film tends to protect aluminum from the more common corrosive elements such as oxygen, carbon dioxide and hydrogen sulfide. This film is sensitive to both high and low pH and extremes of salinity. Consequently, when aluminum drill pipe is being used the pH and Pf of the mud should be maintained within a relatively narrow range as shown in Figure 3. Ideally the pH should fall between 8.6 and 9.8. In addition, aluminum drill pipe should not be used in muds with salt content in excess of 180,000 ppm (204,000 mg/l). If such a condition cannot be avoided then pH must be controlled at 9.5 as an absolute maximum.

SCALE

Scale is a mineral deposit formed under certain system conditions. As a general rule, systems with a high corrosion rate will not be scale forming and vice versa. Factors involved in scale formation are high pH, presence of calcium salts, total solids and temperature. The most common types of scale in a drilling environment are calcium carbonate ($CaCO_3$) and calcium sulfate or gypsum ($CaSO^4$). An iron sulfide scale is occasionally formed in the presence of H_2S.

Scale inhibitors are available commerically and are generally some form of phosphate. While these inhibitors will keep scale from forming, they will not cause removal of scale already deposited. As mentioned before scale can lead to severe corrosion problems and, therefore should be removed mechanically if possible.

CORROSION MONITORING

The corrosiveness of a system can be monitored electronically. Oxygen content and resistivity can be monitored. The most common form of corrosion monitoring used during drilling however, is corrosion coupons.

Drill pipe corrosion coupons are rings machined to fit in the tool joint of a drill pipe. The coupons should be of the same alloy as the pipe and should have the same ID so as to minimize metal loss from erosion.

A normal corrosion ring test consists of two rings, one placed near the collars and one near the kelly usually in the Kelly Saver Sub. The rings should be left in place for a minimum of 40 hours as a shorter period of time may give eroneous results. An optimum time would be 5-7 days. After removal, the rings should be wiped dry, rewrapped and returned to the lab for evaluation. The lab will test for scale formation and weight loss. Corrosion effects are usually reported in terms of weight loss per area per time period such as $lb/ft^2/yr$ or $Kg/m^2/yr$ or occasionally as reduction in wall thickness (mpy). The generally accepted ranges for tolerable corrosion rates are 0-2 $lb/ft^2/yr$, 0-10 $Kg/m^2/yr$ and 0-50 mpy.

While these values are important, the corrosion ring report is not complete without the results of a visual inspection. It is possible to have a severe pitting problem but have it show up as an acceptable corrosion rate due to the relatively small amount of metal loss involved.

SUMMARY

Corrosion problems may become more widespread if the trend toward less highly treated nondispersed mud systems continues. The technology for detection and treatment of corrosion is readily available and easily implemented at the decision of the operator.

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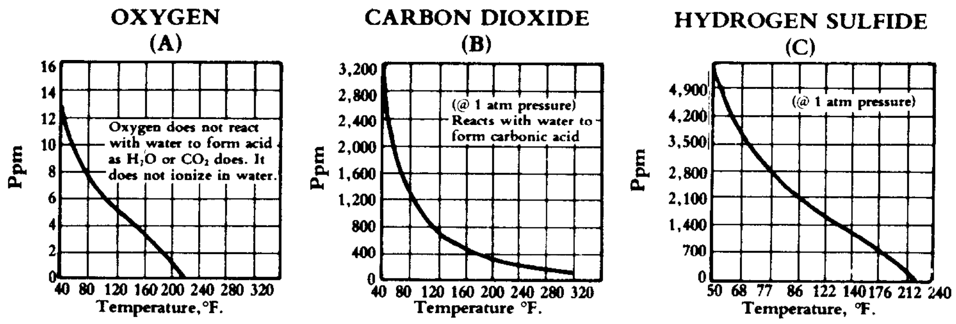

Solubility in Water

FIGURE 1 — SOLUBILITIES OF ACID GASES IN WATER AT VARYING TEMPERATURES

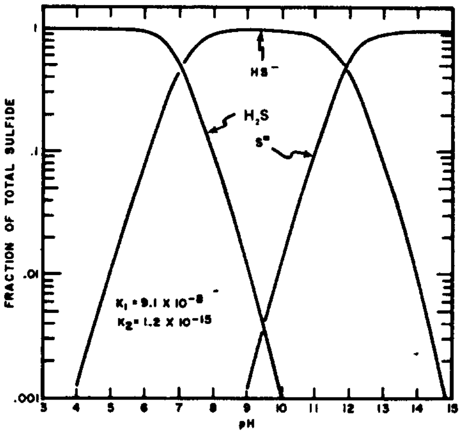

FIGURE 2 — RELATIVE CONCENTRATION OF H_2S BY PRODUCTS IN VARYING pH RANGES

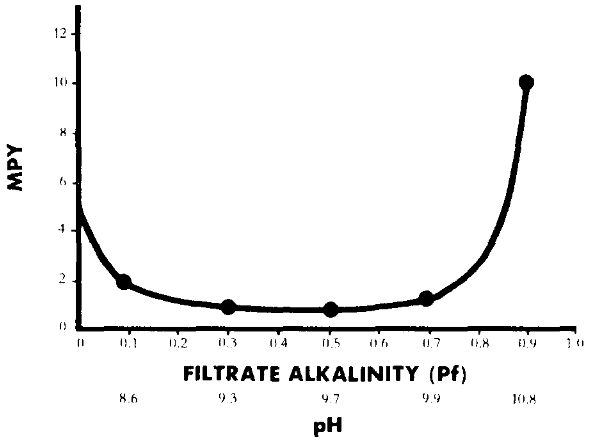

FIGURE 3 — FOUR DAY CORROSION RATE OF ALUMINUM COUPONS IN VARYING pH RANGES

TABLE 1

AVERAGE CORROSION RATES IN UNTREATED MUDS

Fluid Type	Corrosion Rate lb/ft/yr
Freshwater	3-15
Low solids undispersed	3-15
Seawater	15
KCl polymer	15
Sat. sodium chloride	15
Oil muds	<2

TABLE 2

Toxicity of hydrogen sulfide to men

H_2S %	0-2 Min.	2-15 Min.	15-30 Min.	30 Min-1 Hr.	1-4 Hr.	4-8 Hr.	8-48 Hr.
0.005 0.010 50-100 ppm				Mild conjunctivitis; respiratory tract irritation.			
0.010 0.015 100-150 ppm		Coughing; Irritation of eyes; loss of sense of smell.	Disturbed respiration; pain in eyes; sleepiness.	Throat irritation.	Salivation and mucous discharge; sharp pain in eyes; coughing.	Increased symptoms.*	Hemorrhage and death.*
0.015 0.020 150-200 ppm		Loss of sense of smell.	Throat and eye irritation.	Throat and eye irritation.	Difficult breathing; blurred vision; light shy.	Serious irritating effect*.	Hemorrhage and death.*
0.025 0.035 250-350 ppm		Irritation of eyes; loss of sense of smell.	Irritation of eyes.	Painful secretion of tears; weariness.	Light shy; nasal catarrh. pain in eyes; difficult breathing: conjunctivitis.	Hemorrhage and death.*	
0.035 0.015 350-450 ppm		Irritation of eyes; loss of sense of smell.	Difficult respiration; coughing; irritation of eyes.	Increased irritation of eyes and nasal tract; dull pain in head; weariness; light shy.	Dizziness; weakness; increased irritation; death.	Death.*	
0.050 0.000 500-600 ppm	Coughing; collapse and unconsciousness.*	Respiratory disturbances; Irritation of eyes; collapse.*	Serious eye irritation; light shy; palpitation of heart; a few cases of death.	Severe pain in eyes and head; dizziness; trembling of extremities; great weakness and death.*			
0.060 0.070 0.080 0.10 0.15 600-1,500 ppm	Collapse;* unconsciousness;* death.	Collapse,* unconsciousness;* death.*					

*Data secured from experiments on dogs which have a susceptibility similar to men.

Source: National Safety Council data sheet D-chem. 16