ACID CORROSION INHIBITORS: THE EVOLUTION FROM ART TO SCIENCE

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INTRODUCTION

Basically, corrosion is an electrochemical process consisting of an exchange of electrical charges, resulting in the conversion of an active, solid metal into a soluble ionic state. Due to the electrochemical nature of corrosion, thermodynamics must play an active part in the process. This can be seen by observing metals in their natural states. Most metals exist in their natural states as compounds (oxides, sulfides, carbonates, etc). This is their thermodynamically stable state. As an example, Table 1 lists a number of the naturally occurring compounds of iron. In order to fashion useful articles from these iron compounds, the iron must be extracted and converted to the metallic form. Unfortunately, the resulting metallic form is less thermodynamically stable than the original compounds.

When these metal articles are re-exposed to a natural environment (e.g., acid), they tend to revert to their more thermodynamically stable, natural state by "corroding" to form metallic compounds; whereas, less active metals that exist in nature as pure elements (e.g., gold), have excellent corrosion resistance in natural environments. This is because the metallic form is their most thermodynamically stable state. Therefore, it can be concluded that corrosion is possible only if the products of the reaction are more stable than the reactants, see Table 2.

CORROSION MECHANISM

Consider the nature of electrochemical corrosion. In order for electrochemical corrosion to occur, there must be an electrolyte (conducting medium), an anode and cathode, and various chemical reactions occurring at these two areas. In the process, a galvanic cell is produced. (For an interesting discussion of the discovery of galvanic cells and the origin of electrochemistry, see Ref. 1.)

Within the galvanic cell, oxidation reactions occur at the anode and reduction reactions occur at the cathode. Oxidation is the change from an uncharged metal atom to a positively charged metal ion in solution. This reaction leaves negative charges (electrons) that migrate through the metal to the cathode in order to facilitate the reduction reaction. Reduction involves the combination of the transferred electrons with various chemicals in solution. This exchange of electrical charges establishes a potential difference between the two electrodes and results in a measurable electrical current.

A familiar example of such a galvanic cell can be observed in the traditional automobile storage battery. The automobile battery actually develops a harnessable current as the result of the reaction between an electrolyte (sulfuric acid) and a series of alternating anodic (lead) and cathodic (lead dioxide) plates. Here again, oxidation occurs at the anode and reduction occurs at the cathode. As the process continues, the lead plates are slowly dissolved or corroded and eventually the battery can no longer produce a current. Figure 1 illustrates the specific reactions that occur.

Anode Reactions: $Pb^{\circ} \longrightarrow Pb^{+2} + 2e^{-}$ (oxidation)

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$

Cathode Reactions: $PbO_2 + 4H^{+} + 2e^{-} \longrightarrow Pb^{+2} + 2H_2O$ (reduction)

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$

FIG. 1—ELECTROCHEMICAL REACTIONS OCCURRING IN THE AUTOMOBILE STORAGE BATTERY

This same type of electrochemical corrosion occurs when oilfield tubular goods are exposed to various electrolytes (e.g., brines and acids). In the case of large metallic surfaces such as oilfield tubular goods, the presence of anodes and cathodes is less apparent. Actually, numerous anodic and cathodic sites are scattered throughout the iron matrix, the nature of the sites being determined by variations in metallurgical characteristics, heat-treating, impurities, etc. It has been found that these electrode sites shift during the corrosion process. The sites tend to orient themselves so as to set up a multiplicity of miniature galvanic cells or "local-action cells" on the metal surface. The presence of these cells can be demonstrated by using a ferroxyl indicator described by Evans.[2] This indicator is composed of two chemicals, one of which forms a deep blue coloration upon contacting soluble iron ions (formed at the anodes) while the other chemical forms a pink coloration upon contacting hydroxide ions (formed at the cathodes). When steel is immersed in a salt-water solution containing oxygen and this indicator, the anodic sites turn blue and the cathodic sites turn pink. In both brine-water corrosion and acid corrosion, the most detrimental effects are observed at the anodic sites, because it is here that dissolution of the iron actually takes place, as the ferroxyl indicator so vividly demonstrates.

In the case of brine-water corrosion, metallic iron is oxidized at the anodic sites to form positively-charged iron ions which in turn combine with negatively-charged chloride ions as well as oxide and hydroxide ions which are formed at the cathodic sites as the result of the reduction of oxygen. The result is good old-fashioned rust. For a more detailed description of the reactions, see Fig. 2.

Anode Reaction: $\overset{\circ}{Fe} \longrightarrow Fe^{+2} + 2e^-$ (oxidation)

Cathode Reaction: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (reduction)

FIG. 2—ELECTROCHEMICAL REACTIONS OCCURRING DURING BRINE WATER CORROSION

In the case of downhole hydrochloric acid corrosion, metallic iron is oxidized at the anodic sites to form iron ions which combine with negatively-charged chloride ions to form ferrous chloride (as opposed to ferric chloride, which may form later as the acid is brought to the surface and oxidized[3]). Subsequently, positively-charged hydrogen ions from the hydrochloric acid are reduced at the cathodic sites to form hydrogen gas. This hydrogen gas evolution is the bubbling phenomenon which is observed when iron is immersed in an acid medium. For more details of the reactions, see Fig. 3.

Anode Reaction: $\overset{\circ}{Fe} \longrightarrow Fe^{+2} + 2e^-$ (oxidation)

Cathode Reaction: $2H^+ + 2e^- \longrightarrow H_2$ (reduction)

FIG. 3—ELECTROCHEMICAL REACTIONS OCCURRING DURING ACID CORROSION

Having established the nature of electrochemical corrosion, let us now proceed to consider two of the basic means of mitigating this corrosion, namely, cathodic protection and chemical corrosion inhibitors.

CORROSION INHIBITION BY CATHODIC PROTECTION

One of the earliest approaches to corrosion prevention or inhibition was offered by Sir Humphrey Davy, the British chemist who is generally considered to be the first recognized corrosion chemist. He was assigned the task of devising a means for preventing the corrosion of the copper sheathing of His Majesty's warships. He found that he could prevent this corrosion by attaching blocks of iron to the hulls of the ships. From laboratory experiments, he observed that sea water selectively attacked the iron blocks as opposed to the copper sheathing. This is probably the earliest recorded example of cathodic protection. Unfortunately, however, Davy was unaware that cathodically-protected copper is subject to fouling by marine organisms and as it turned out - the barnacles got him!

Empirical observations had led Davy to this discovery. At the time, he was uncertain as to the mechanism of this phenomenon. What he had actually done was to galvanically connect the copper sheathing, which he was attempting to protect, to a more active metal, namely iron. Iron, having a higher oxidation potential (i.e., a stronger tendency toward oxidation) than copper, was selectively oxidized or corroded and thus became a "sacrificial anode". (In a similar manner, a less active material (e.g. carbon) is often used as an "auxiliary anode" by employing a weak external current.) See Table 1 for a listing of the standard oxidation potentials of a number of common metals.

TABLE 1—NATURALLY OCCURRING IRON COMPOUNDS

Mineralogical Name	Chemical Formula	Occurrence
Hematite	Fe_2O_3	Sandstone
Magnetite	Fe_3O_4	Granite
Pyrite	FeS_2	Sedimentary rock
Pyrrhotite	FeS	Sedimentary rock
Siderite	$FeCO_3$	Limestone

Today, cathodic protection of this sort finds a number of commercial applications including sacrificial magnesium inlet tubes in steel hot water heaters as well as the cathodic protection of underground pipelines and surface storage tanks.[4] In the oil industry, cathodic protection finds application in preventing corrosion of well casing, pipelines, and offshore platforms.

When current flows between an anode and cathode, the potentials of both change. Their respective potentials tend to approach one another according to strict electrochemical laws. This shifting of the electrode potentials toward each other is termed polarization. Polarization tends to reduce the potential difference between anode and cathode areas, thus reducing the driving force for the corrosion reaction. Anything that can be done to increase the polarization of either the anodic or cathodic areas will subsequently decrease the corrosion.

Polarization is often the result of either an insufficiency of the desired species or an excess of the unwanted species at the electrode site. When iron corrodes in hydrochloric acid, hydrogen ions are reduced at the cathode to form hydrogen gas. Once formed, the molecule of hydrogen is no longer needed by the corrosion reaction. In fact, as long as it remains in the cathodic area, it tends to interfere with the corrosion process by preventing other hydrogen ions from reaching the metal surface and reacting. Hydrogen gas can therefore retard, or polarize, the cathodic reaction. Unfortunately, in heated acid samples, convection currents alone are usually sufficient to sweep away hydrogen molecules, thus permitting the continuation of the cathodic reduction reaction.

CORROSION INHIBITION USING CHEMICAL INHIBITORS

Various chemicals, both organic and inorganic, have been shown to cause varying degrees of anodic or cathodic polarization. These chemicals function by forming a physical barrier against current flow either by plating-out, precipitating, or forming an impervious film on the metal surface.

Inorganic Inhibitors

The inorganic corrosion inhibitors may be divided into anodic and cathodic inhibitors, based upon the type of polarization which they initiate. Anodic inhibitors include various compounds such as chromates, phosphates, silicates, nitrites, and iodides. These materials, which are often used in commercial cooling systems (e.g., automobile radiators), possess the inherent disadvantage of being very concentration-sensitive. Consequently, they must be used in a closed system at high concentrations, or severe pitting corrosion may result.

Cathodic inhibitors include various salts of zinc, nickel, copper, arsenic, antimony, and various other metals. Of particular interest to the oil industry are the arsenic compounds. It has long been observed that a number of arsenic compounds, when added to an acidic solution, have a tendency to plate out metallic arsenic onto the cathodic sites of exposed steel surfaces and decrease the hydrogen evolution, thereby severly limiting the corrosion. From an electrochemical standpoint, it becomes apparent that arsenic compounds tend to act just the opposite of metallic iron when both are placed in acid media. Iron tends towards oxidation from the metallic state to the soluble ionic state; whereas, the arsenic compounds tend toward reduction from the soluble ionic state to the metallic state.

Arsenic compounds have long been used as hydrochloric acid inhibitors in the oil field. Some "old-timers" even insist that the commonly used hydrochloric acid strength, namely 15%, was firmly established in the industry as the result of the hydrochloric acid strength limitation of arsenic corrosion inhibitors (i.e., arsenic inhibitors are ineffective in hydrochloric acid strengths of greater than 17%). Aside from this hydrochloric acid strength limitation, arsenic inhibitors pose numerous other inherent disadvantages including: obvious health hazards, ecological problems, refinery catalyst poisoning at ppm concentrations, and of particular concern, the formation of insoluble arsenic sulfide precipitates when arsenic-inhibited acid contacts hydrogen sulfide gas. Due to their extremely poor solubility characteristics, these precipitates can cause severe permeability damage to viable wells.

The arsenic sulfide precipitation hazard is especially interesting in the light of some recent findings regarding this reaction with hydrogen sulfide.[5] For years, the products of this reaction were believed to be As_2S_3 (orpiment) and in some cases As_4S_4 (realgar). These two arsenic sulfide compounds are known to form upon reaction between the traditional arsenic inhibitors in hydrochloric acid and hydrogen sulfide gas produced by sour wells. Union Oil Co. of California studies have shown that these two arsenic compounds, under the constraints of time, heat, and pressure, tend to convert to another little-known arsenic sulfide compound, namely As_4S_3 (β -dimorphite). Union researchers further observed that this material, as do the other arsenic sulfide compounds, tends to sublime (i.e., convert directly from a solid to a vapor upon heating) and "creep" through the formation and out into the wellbore where it condenses on cooler surfaces, and thus acts as a plugging agent. In a number of deep wells in the Anadarko Basin of Oklahoma, Union observed massive deposits of all three sulfides throughout the tubular goods and even in the surface equipment.

Organic Inhibitors

The majority of the chemical corrosion inhibitors used in the oilfield today are organic compounds. Generally speaking, the organic corrosion inhibitors are more versatile and pose fewer inherent objections than do the inorganic corrosion inhibitors.

Basically, organic inhibitors are composed of rather complex hydrocarbon units with one or more polar groups composed of elements from the fifth or sixth groups of the elemental periodic chart, namely sulfur, oxygen, or nitrogen. These rather complex molecules are constructed so as to maintain a very fine solubility balance when added to the corrosive medium. Organic acid corrosion inhibitors, for example, must be acid dispersible; but not overtly soluble, else they lose their affinity for metallic surfaces. A number of "inhibitor solubilizers" have been employed in the petroleum industry, with varying degrees of success, in attempting to strike this solubility/dispersibility balance.

A number of theories have been proposed in an effort to elucidate the inhibition mechanism of these organic inhibitors. The majority of these theories are too complex to be dealt with here. Suffice it to say that these organic compounds tend to physically or chemically adsorb onto the metal surface, establishing a physical barrier to continued corrosion. One popular theory of interest in a later discussion involves the formation of positively-charged onium ions.[6] This theory states that these polar compounds have a tendency to form positively-charged sulfonium, ammonium, or oxonium ions when added to acid media. In this ionic form, the inhibitors are attracted to and adsorbed at the cathodic sites. Consequently, they serve as cathodic polarizers by limiting hydrogen ion mobility at the cathodes.

One inherent limitation of organic acid corrosion inhibitors is their tendency toward in situ degradation (i.e., they tend to chemically degrade with time in the presence of the corrosive medium). The chemical structure of these materials is altered as a result of their exposure to the corrosive environment. Further studies are currently underway in an attempt to elucidate the mechanism of this degradation process.

INHIBITOR MYTHS AND STOP-GAP MEASURES

As is the case with any evolutionary process, the development of acid corrosion inhibitors has taken place in quantitative leaps followed by periods of relative calm. These leaps represent meaningful breakthroughs in research, while the periods of calm are spent in refinement and extension of these breakthroughs. Until recently, corrosion research had experienced a prolonged period of calm during which a major breakthrough was sorely needed. In an effort to bridge this rather unproductive chasm, a number of inhibitor myths and stop-gap measures appeared on the horizon. Some of these measures were useful, but the majority of them were of rather limited value. These rather questionable practices included: double inhibiting, inhibitor slugs, inhibitor extenders or intensifiers, acid blends, and sulfide control additives.

Double inhibiting is the erroneous concept, held by some, which reasons that if "x" amount of inhibitor provides "y" level of corrosion protection, then "2x" amount of inhibitor should provide a "2y" protection level. In other words, twice as much inhibitor should provide twice as much protection. This is just not the case. Very few acid corrosion inhibitors have protection levels which are straight-line functions of concentration. In addition, in the case of organic acid corrosion inhibitors, these particular materials have a specific concentration limit, above which no additional protection is obtained. This concentration limit varies from inhibitor to inhibitor; but as a general rule of thumb, 3% concentrations (i.e., 30 gal./1000 gal. of acid) should be close to the concentration limit for most organic acid corrosion inhibitors.

Inhibitor slugs (i.e., concentrated doses of corrosion inhibitor) are sometimes pumped into wells ahead of subsequent acid treatments. This is reportedly done in order to lay down a protective film on the metal surface prior to the acid exposure. Two problems arise here. To begin with, many organic acid corrosion inhibitors are not fully "activated" (i.e., do not form onium ions) until they are added to acid. Consequently, an inferior film is being formed on the metal surface by the straight inhibitor. In addition, acid corrosion inhibition is a dynamic process. The protective film that forms on the metal surface tends to degrade and must therefore be continually replaced by fresh, undegraded inhibitor from the acid medium in order to provide adequate protection.

Extenders or intensifiers for organic acid corrosion inhibitors have been shown to offer some degree of additional protection when used in conjunction with organic inhibitors in acid solutions.[7] These extenders or intensifiers are composed of organic and inorganic materials which function synergistically with common organic inhibitors. It is believed that these materials react either with the organic inhibitor or with the metal surface in forming a more effective corrosion barrier than that offered by the organic inhibitor alone. Laboratory tests have demonstrated that many of these materials do provide increased inhibition levels. However, their high cost and objectionable side effects often preclude their application. Some of these materials have very poor acid solubilities, and their acid solutions must often be heated in order to solubilize them. In addition, at least one commercially available intensifier tends to form an insoluble precipitate upon contacting hydrogen sulfide gas.

Acid blends have been used in the oilfield for a number of years and for a number of reasons; one reason being their decreased corrosion levels. Mixtures of organic acids (e.g., acetic and formic acids) with hydrochloric acid have found wide-ranging application in extremely corrosive environments. However, these acids blends are known to have a limited rock-dissolving capacity as compared with straight hydrochloric acid. Today, these blended acids are being replaced by straight hydrochloric acid preceded by a cooling pad fluid.

Sulfide-control additives might well fall into the category of second generation stop-gap measures in that they are often used in an effort to offset the detrimental side effects of other stop-gap measures such as inhibitor intensifiers which precipitate upon contacting hydrogen sulfide. These sulfide-control additives are often added to acid treatments in an effort to "tie up" extraneous sulfide ions and thus prevent their reaction with the sulfide-sensitive inhibitor intensifier. Unfortunately, one would need an uneconomically large dose of these sulfide-control agents in order to "tie up" all incoming sulfide ions produced in many sour wells.

CURRENT RESEARCH TRENDS

Having touched on the theory and recent history of acid corrosion inhibitor development, let us now take a brief look at some of the current research trends in the area of acid corrosion technology.

Recent research efforts have brought to light a number of interesting concepts of value not only to future research programs but also in the current field application of acid corrosion inhibitors. One of the more fruitful areas of acid corrosion research has been the study of pertinent corrosion test parameters. These studies have elucidated new test parameters which are critical to the understanding and development of new acid corrosion inhibitors; parameters such as inhibitor-to-coupon surface area ratios, test pressures, types of steel coupons employed, and methods of coupon pretreatment. It is now known, for instance, that larger test cells often generate lower corrosion rates at comparable inhibitor concentrations and coupon sizes. This is merely the result of the availability of more inhibitor (be it the same inhibitor concentration employed in a smaller test cell) to the same amount of metal surface area. It is also now well established that some inhibitors are pressure-sensitive and that most inhibitors offer varying levels of inhibition depending on the type of test coupon materials employed (e.g., N-80 tubing, P-105 casing, C-75 tubing, Nowsco coiled tubing, etc.). And finally, some inhibitors perform better under mildly turbulent conditions while others are severely affected by such turbulence.

Due to the nature and significance of these parametric variations, it should be apparent that complete knowledge of individual well conditions and downhole environments would be extremely useful in the selection and effective application of acid inhibitors. Where possible, this information should be made available to those individuals who are responsible for preparing well treatment recommendations.

In contemplating the significance of these corrosion test parameter variations, it soon becomes apparent that acid corrosion tests can easily be devised to optimize the test results for a specific inhibitor based on its individual characteristics. It also becomes apparent that industry-wide standardization of test equipment and test procedures is in order. Efforts toward the latter are currently being undertaken by an American Petroleum Institute - National Association of Corrosion Engineers joint subcommittee chairmanned by D.R. Fincher of Fincher Engineering Co. of Houston and under the oversight of C.O. Liles of the API Division of Production office in Dallas. This committee has already set up some tentatively standardized test procedures and has designed, and is currently testing, a small corrosion test vessel hopefully for eventual industry-wide standardization purposes. Details regarding these standardization efforts as well as specific information concerning the test procedures and test equipment can be obtained by contacting Mr. C.O. Liles at the API office in Dallas. It may well be that this committee is in the process of taking one of the much-needed quantitative leaps in the evolution of acid corrosion inhibitors.

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TABLE 2 — STANDARD OXIDATION POTENTIALS OF COMMON METALS

Reaction	E_o (volts)
$\overset{\circ}{K} \longrightarrow K^+ + e^-$	+ 2.925
$\overset{\circ}{Ca} \longrightarrow Ca^{+2} + 2e^-$	+ 2.87
$\overset{\circ}{Na} \longrightarrow Na^+ + e^-$	+ 2.714
$\overset{\circ}{Mg} \longrightarrow Mg^{+2} + 2e^-$	+ 2.37
$\overset{\circ}{Al} \longrightarrow Al^{+3} + 3e^-$	+ 1.66
$\overset{\circ}{Zn} \longrightarrow Zn^{+2} + 2e^-$	+ 0.763
$\overset{\circ}{Fe} \longrightarrow Fe^{+2} + 2e^-$	+ 0.44
$\overset{\circ}{Ni} \longrightarrow Ni^{+2} + 2e^-$	+ 0.250
$\overset{\circ}{Pb} \longrightarrow Pb^{+2} + 2e^-$	+ 0.126
$\overset{\circ}{H}_2 \longrightarrow 2H^+ + 2e^-$	0.000
$\overset{\circ}{Cu} \longrightarrow Cu^{+2} + 2e^-$	- 0.337
$\overset{\circ}{Ag} \longrightarrow Ag+ + e^-$	- 0.7991
$\overset{\circ}{Au} \longrightarrow Au^{+3} + 3e^-$	- 1.50

↑ Increased tendency towards oxidation

↓ Increased tendency towards reduction