Theories of Corrosion and Corrosion Inhibitors

By PARKE D. MUIR
Dowell Division of the Dow Chemical Company

INTRODUCTION

The word corrosion may be defined as the destruction of metal by chemical or electrochemical action. Destruction by mechanical means is usually called erosion. The rusting of iron is an example of corrosion, while the filing of iron to dust is an example of erosion.

Essentially, atmospheric corrosion is the reverse process to that involved in refining metals from their ores. Iron is usually found in nature as iron oxide or iron hydroxide. When it corrodes in air, it returns to iron oxide or iron hydroxide. Copper occurs as the sulfide or basic sulfate. When copper tarnishes, it reverts to the sulfide, and, in certain atmospheres, to the basic sulfate.

Because the refining of metal from ore requires the expenditure of energy, the metal is at a higher energy level than the ore, and it is natural that it would try to revert to the form in which it is found in nature. Because iron need only combine with oxygen to form iron oxide, or with oxygen and water to form the hydroxide, it is a wonder that we can use iron at all when it is exposed to air. The main reason that it does not destroy itself more quickly than it does is that rust, as it forms on the metal, acts as a barrier between the metal and air, thus slowing down the corrosion process.

ELECTROCHEMICAL THEORY OF CORROSION

Let us now examine this corrosion process and try to understand the electrochemical reaction that causes corrosion. An electrochemical reaction could be defined as one in which there is a chemical change and a flow of electric current. In some types of corrosion, this current can be measured rather easily, while in others it is virtually impossible to detect. However, in most cases, it is possible to establish that a current does flow and the direction of its flow.

Two chemical reactions occur during corrosion. One, termed oxidation, occurs at the anode, where metal changes from solid, electrically neutral atoms into positively charged ions. The other reaction, called reduction, occurs at the cathode, where some substance in solution changes to a form less positively charged. An example of iron corrosion, when coupled with copper in a salt water solution containing oxygen, will serve to illustrate these reactions. At the anode (iron), the oxidation reaction will occur and may be written as follows:

$Fe^- \rightarrow Fe^{++} + 2e^-$ (iron - a neutral material going into solution as a positively charged ion and leaving behind two negatively charged particles or electrons)

Electrons travel through the metal to the cathode (copper), where they enter into the reduction reaction. In this particular case, the reduction reaction occurring at the cathode may be written as follows:

$2e^- + H_2O + \frac{1}{2}O_2 \rightarrow 2OH^-$ (a case of two neutral materials combining with electrons to become negatively charged ions)

If these same two metals were connected in an acidic solution, the reaction occurring at the cathode would be written as follows:

$2e^- + 2H^- \rightarrow 2H^\circ \rightarrow H_2\uparrow$ (positively charged hydrogen ions receiving electrons and becoming a neutral or uncharged material)

In the above example, the copper is said to be more noble than the iron, and it is cathodic in relation to iron. In other words, of these two metals, the iron has a greater tendency to give up electrons and enter the solution than does copper. In the case of iron coupled to magnesium in the same situation, the iron would be the cathode and the magnesium the anode.

It is not necessary that two different metals be coupled together in order to have anodic and cathodic areas. It has been proved conclusively that corrosion occurring on a single piece of metal is also electrochemical in nature and that anodes, cathodes, and current flow are present. One of the most common examples is that of iron and its oxide.

In this case, the area covered with oxide is cathodic to the bare metal. Steel with mill scale present will corrode rapidly if the mill scale is removed from a small area and a large area of the steel is left covered with scale.

It should be understood that, while the examples given have indicated a solution as the electrolyte for the current to flow through, the earth can also act as an electrolyte, and that similar reactions can and do occur in the case of metal buried in the earth.

It has been shown that the amount of corrosion occurring (amount of metal that is being converted to ionic form) is directly proportional to the amount of current that flows between the anode and cathode.

As a corrosion process continues, certain things tend to stifle or slow down the reaction. For example, when a reaction occurring at the cathode yields an insoluble product, the product will tend to keep fresh chemicals from reaching the surface of the metal to accept the electrons. As a result, the corrosion process will be slowed. If chemicals are present which immediately react with the metal as it goes into solution at the anode, producing an insoluble product, this will stifle the corrosion.

On the other hand, if the anodic reaction yields a soluble product and a large supply of chemicals is present to act as electron acceptors (such as hydrogen ions in acid solutions) and, if no insoluble product is formed at the cathode, the corrosion process will not tend to stifle itself.

FACTORS INFLUENCING CORROSION

Many factors affect the amount of corrosion that occurs. Some of these factors are the corrosive tendency of the metal involved, the environment, the nature of the corrosion products, and the other metals involved.

Corrosive Tendency of the Metal Involved

All metals have a certain tendency to corrode in a particular environment. The electromotive series (abbreviated in Table 1) provides a rough measure of the tendency for metals to corrode or revert to their native state, but these relative positions are not the same under all environments.

Environment

The environment plays a very important part in the corrosion process. Several divisions of the environment will be discussed in order to cover this subject thoroughly.

pH or Acidity of Solution

Because most corrosion reactions use up hydrogen ions, the acidity of a solution, as represented by hydrogen ion concentration (pH), is a very important factor. In general, the more acid solutions (lower pH) are more corrosive than alkaline (high pH) solutions.

Velocity

An increase in velocity of a fluid through a pipe tends to accelerate corrosion. This is brought about by two factors. Stifling films which might be formed are more readily removed, allowing corrosion to continue, and the rate at which corrosive chemicals are brought to the surface of the metal is increased.

Oxygen

Oxygen, in general, tends to accelerate corrosion. It is believed that this is principally due to its reaction at the cathode, aiding in removing electrons and allowing the corrosion process to continue.

Temperature

The rate of corrosion tends to increase with rising temperature, but several factors may cause this not to be true in some cases. For example, oxygen becomes less soluble in water at higher temperatures; if oxygen were one of the main factors in a certain corrosive environment, an increase in temperature to near the boiling point of water might decrease corrosion. Other examples of less corrosion at higher temperatures could occur by the precipitation of protective coatings, such as calcium carbonte.

Reaction Products

If the reaction products from corrosion form tightly adhering, closely packed films on the metal, corrosion will be stifled quite effectively. The oxide film on aluminum which makes it resist atmospheric corrosion is an example of such a film. If the reaction products are soluble or if they form loosely packed deposits, corrosion will not be stifled and may actually be accelerated in localized areas.

Other Metals Involved

If dissimilar metals that are far apart in the electromotive series are joined together without insulation, the less noble metal will corrode, while the more noble one will be protected. If the less noble one has the smaller area, it may corrode quite rapidly.

CORRECTIVE MEASURES

There are a number of corrective measures which may be taken to control corrosion. Each such measure has its advantages under certain conditions.

One corrective measure is to use more corrosion-resistant metals. For certain problems, this is the best solution. Protective coatings can be used. An additional solution to the problem is to alter the electrolyte until it is no longer corrosive, such as by neutralizing acid solutions. The metal can be replaced with some other substance, such as cement, transite, tile, plastic, or other non-metallic material.

Another corrective measure is that of cathodic protection, whereby electric current is used to reduce corrosion. This current may be supplied by sacrificial anodes such as magnesium or by the use of rectifiers. The use of corrosion inhibitors is another method. When added to the corrosive environment in very small quantities, they act to suppress the corrosion reaction to a small fraction of that which would normally take place. The use of corrosion inhibitors makes it possible to use strong acid solutions for cleaning scale from steel piping. Without inhibitors, this would have been impossible.

The rest of this paper will be concerned with some of the theories of corrosion inhibitors, the different types of inhibitors and how they differ from each other.

CORROSION INHIBITORS

Mechanism of Inhibitor Action

Corrosion inhibitors may be classified in a number of different ways, depending on their composition and how they function. Basically, they can be divided into two main classifications: inorganic and organic.

Inorganic Inhibitors

The inorganic inhibitors may be subdivided into anodic and cathodic inhibitors by their action. As was pointed out earlier, there are two reactions which occur in corrosion. At the anode, metal goes into solution. At the cathode, electrons are discharged. Corrosion can be reduced by slowing down or stopping either of these reactions. Inhibitors that retard the anodic reactions of corroding metals are classified as anodic inhibitors, while those which retard the cathodic reactions are classified as cathodic inhibitors.

Some typical inorganic anodic inhibitors are sodium chromate, sodium dichromate, sodium hexametaphosphate, sodium nitrite and sodium silicate. These usually act as anodic inhibitors, although in some instances they may serve as cathodic inhibitors as well.

There are two main theories regarding the manner in which inorganic anodic inhibitors function: one, by the formation of a protective, insoluble film on the metal; the other, by the adsorption or chemisorption of the inhibitors onto the metal surfaces. According to Evans[1], most sodium or potassium salts containing anions which form a sparingly soluble salt with the metal under consideration, act as anodic inhibitors. For instance, sodium phosphate in neutral or alkaline solutions acts by the precipitation of iron phosphate at the anode, where the iron dissolves. In a similar manner some of these inorganic inhibitors cause a thin protective film of iron oxide to form on the surface of the steel.

A theory that the precipitation of a film, such as iron oxide or iron phosphate, is not necessary for inhibition, although such a film may halp the overall protection, is subscribed to by Uhlig[2]. According to this theory, inhibition by chromates and other oxidizing inhibitors is due primarily to chemisorption.

The metal atoms remain in place on the metal but since these have valence forces which need to be satisfied, negative ions, such as chromates, are adsorbed to the metal and form surface compounds in place[3].

This is in contrast to the precipitation of a film by dissolved iron reacting with the anion and then being deposited on the metal. Of course, both systems can operate in the same medium.

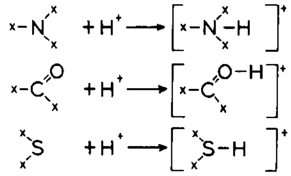
Inorganic cathodic inhibitors are those inhibitors that slow down the cathodic reaction. Typical cathodic inhibitors for iron, in neutral solutions containing oxygen, are salts of zinc and nickel. The action of these materials is probably due to their forming insoluble hydroxides at the cathodic areas where hydroxyl ions are formed . Salts of arsenic and antimony act as cathodic inhibitors in acid solutions. It is believed that these are plated onto the cathodic areas as free metal and decrease the hydrogen evolution, thereby limiting the corrosion.

Organic Inhibitors

Most of the inhibitors in use to prevent oil well and refinery corrosion are organic inhibitors. Generally speaking, the organic inhibitors do not undergo chemical changes during inhibition, whereas many of the inorganic inhibitors do.

Inhibitors of the organic type are, almost without exception, compounds containing elements of the fifth or sixth groups of the periodic table. Most of these inhibitors contain sulfur, oxygen, or nitrogen . Such organic inhibitors usually consist of a polar group (which is the end of the molecule containing either nitrogen, sulfur or oxygen) attached to a long chain of saturated hydrocarbons.

A popular theory regarding the functioning of such inhibitors has been that these organic semipolar compounds were adsorbed at the cathodic areas. Considerable evidence is available to support this theory. One particular theory is that such compounds have a tendency in acid solutions to form ions of the ammonium, oxonium or sulfonium type, as shown:



Mann and his co-workers [4] [5] [6] proposed that in this ionic form, the inhibitors are attracted to and adsorb at the cathodic areas, since these areas are negatively charged. Since they cannot be electrically discharged (as hydrogen could be, for example) they remain adsorbed and prevent hydrogen ions from discharging at the cathodes, thus inhibiting corrosion by cathodic polarization. Mann and his co-workers showed that inhibition increased with chain length and cross section of the molecule, and several other investigators supported Mann's conclusions.

Recently, the theory of cathodic adsorption of inhibitors of this type has been questioned. Hoar[7] has observed a shift of the electrode potential toward more cathodic values which indicate anodic polarization, or that the inhibitors were being adsorbed anodically. Other studies have shown both anodic and cathodic polarization with these inhibitors indicating overall general adsorption.

Hackerman and Makrides[8] proposed that adsorption takes place generally, rather than specifically at either anodic or cathodic areas. One explanation is that, like the theory mentioned on inorganic inhibitors, the surface of the metal has some valence forces that must be satisfied. Thus, it may be that the binding forces responsible for the strong attraction of these inhibitors is the formation of a dative bond between the metal and the organic molecule. Such bonds are formed through sharing a pair of electrons between the inhibitor and the metal. This has been postulated by George and Hackerman[9].

Laboratory studies have shown that many inhibitors are adsorbed very strongly. For example, Hackerman and George made studies in which inhibitors were adsorbed from benzene solutions onto metal coupons. The specimens were then washed with fresh benzene and placed in hydrochloric acid solutions. The investigators found that many inhibitors continued to furnish protection, even though there was no opportunity for replacement of the inhibitor.

Many others have made similar studies. One good example is the standard NACE laboratory screening test for inhibitors. In this test, oil soluble organic inhibitors are adsorbed during a 10-second time interval, after which the metal specimens are subjected to a corrosive solution for 7 days. The protection given by some inhibitors tested under these conditions is greater than 90 per cent. These tests would indicate that, whatever the forces involved in the holding of the inhibitor on the metal, they are in some cases very strong.

Another illustration that inhibitor film is firmly held, even without replacement of the film, is that many producing wells are now being treated with organic inhibitors only once a week, yet these wells are being protected from corrosion during the interim between applications.

Experiments made in pumping wells have indicated that the inhibitor, in most cases, comes in contact with rods and tubing for only a relatively short interval of time. Since protection is maintained between treatments, it follows that the adsorbed film must remain tightly held for some length of time. Extensive research study is in progress to find materials with even stronger attractive forces than those presently being used.

SUMMARY

There are several theories regarding the manner in which inhibitors function. In many inhibitors a general adsorption, cathodic and anodic adsorption, chemisorption and physical adsorption, and preferential oil wetting, probably all combine to provide the corrosion protection. These mechanisms can reinforce each other and in most inhibitor applications, it is believed that more than one mechanism is involved.

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