ZETA CORPORATION

GENERAL INFORMATION REGARDING METAL CORROSION & PASSIVATION

pas.siv.ate \’pa-si-,vat\ *vt* **–at.ed; -at.ing (1)** to make inactive or less reactive <~ the surface of steel by chemical treatment> **(2)** to protect (as a solid state device) against contamination by coating or surface treatment .

co.ro.sion \ kə-rōˈzhən\ *n* (**1a)**. The act or process of corroding. (**b**) The condition produced by corroding**.** **(2)** A substance, such as rust, formed by corroding**.**

cor.rode \ kə-rōdˈ\ (**1)** To destroy a metal or alloy gradually, especially by oxidation or chemical action: *acid corroding metal.*

Fluid Corrosion: General

Pure metals and their alloys tend to enter into **chemical** union with the elements of a corrosive medium, such as water, to form stable compounds similar to those found in nature. When metal loss occurs in this way, the compound formed is referred to as the **corrosion product** and the metal surface is spoken of as being **corroded.**

In most aqueous systems, the corrosion reaction is a three-step process divided into an anodic portion and a cathodic portion.

1. Loss occurs from that part of the metal called the anodic area (anode) where the metal is lost to the water solution into its oxidized ion.
2. As a result of this oxidized ion, electrons are released to flow through the metal to the cathodic are (cathode).
3. Oxygen in the water solution moves to the cathode and completes the electric circuit by using the electrons that flow to the cathode to form hydroxyl ions (OH-) at the surface of the metal.

Polarization-Depolarization

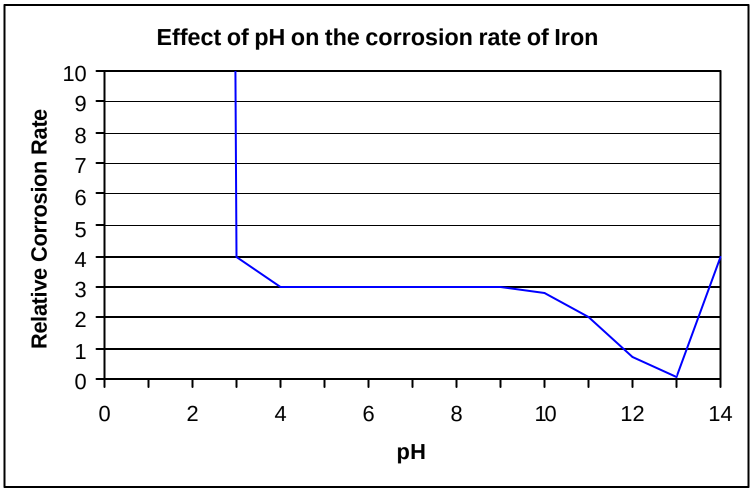
As a result of the corrosion reaction hydroxyl ions (OH-), hydrogen gas (H2), or both, are produced at the cathode. If these chemical reaction products remain at the cathode they produce a barrier that slows the movement of oxygen gas or hydrogen to the cathode. This barrier becomes a corrosion inhibitor because it insulates or physically separates oxygen in the water and the electrons at the metal surface. The formation of this physical barrier as a result of corrosion is called ***polarization***. The removal or disruption of this barrier exposes the cathode, and corrosion resumes. This action, called ***depolarization*** is enhanced by lowering the pH of the water or by increasing the water velocity in to the turbulent flow region.

Pitting Corrosion. Pitting is a form of corrosion that develops in highly localized areas on the metal surface. This results in the development of cavities or pits. They may range from deep cavities of small diameter to relatively shallow depressions.

Corrosion Rates.

Preventing any one of the three steps involved in the corrosion process would cause the process to stop. The slowest of the three steps determines the rate of the overall corrosion process. The cathodic (step 3) is the slowest of the three steps involved in the corrosion of steel, thus this reaction determines the corrosion rate. Corrosion inhibitors are designed to stop or reduce the anodic reaction, the cathodic reaction or both.

Factors Influencing Corrosion



Solution pH. The corrosion rate of most metals is affected by pH. Acid-soluble metals such as Iron have a relationship as shown in figure 1. In the middle pH range (~ 4 to 10), the corrosion rate is controlled by the rate of transport of oxidizer (usually dissolved O_2) to the metal surface. When pH values can be modified, it will generally be beneficial to hold the acid level to a minimum. As it can be seen in the graph, alkaline pH values are less critical than acid values with respect to controlling corrosion.

Dissolved Solids.

The influence of dissolved solids on Corrosivity is very complex. Not only is the concentration important, but also the species of ions involved. Some solids such as carbonate and bicarbonate may reduce corrosion, whereas others such as chlorides and sulfates may increase it by interfering with protective films.

Suspended Solids

The presence of suspended solids has the potential to produce ***concentration cell corrosion*, a** type of corrosion that occurs when a single metal is exposed to different concentrations (ionic strengths) of water solutions.

In a cooling system a deposit may form on a clean metal surface. The oxygen under this deposit will be consumed by the normal corrosion reaction. As the oxygen under the deposit is depleted, an oxygen gradient is created with respect to the water surrounding the deposit because fresh oxygen from the bulk solution cannot migrate through the deposit. Under these conditions the area under the deposit becomes anodic with respect to the surrounding areas and an oxygen differential cell is created.

Temperature. The rate of corrosion tends to increase with rising temperature. Temperature also has a secondary effect through its influence on the solubility of Oxygen.

Velocity. An increase in the velocity of relative movement between a corrosive solution and a metallic surface frequently tends to accelerate corrosion.

Films. Once corrosion has started, its further progress very often is controlled by the nature of films, such as ***passive films***, that may form or accumulate on the metallic surface. The classical example is the thin ***oxide film*** that forms on stainless steels.

Insoluble corrosion products may be completely impervious to the corroding liquid and, therefore, completely protective; or they may be quite permeable and allow local or general corrosion to proceed unhindered.

It is agreed generally that the characteristics of the ***rust films*** that form on steels determine their resistance to atmospheric corrosion. The rust films that form on low-alloy steels are more protective than those formed on unalloyed steels.

In addition to films that originate at least in part in the corroding metal, there are others that originate in the corrosive solution. These include various salts, such as carbonates and sulfates, which may be precipitated from heated solutions, and insoluble compounds, which form on metal surfaces in contact with certain specific products such as biofilms.

CORROSION INHIBITION

In water distribution systems the goal is control corrosion levels within tolerable levels. This can be achieved by selecting the appropriate materials of construction, good design practices and a proper water treatment program.

To control corrosion one must stop or slow down one of the three steps involved in the corrosion process mentioned above. One way in which this can be done is by ***selecting materials*** with low corrosion potentials such as stainless steel, titanium, PVC and special alloys. However, it is not always economically feasible to do so, or the conditions of the water prevent the use of such materials.

Coatings and linings is another practical way to protect metal surfaces by applying a physical barrier between the metal and the fluid. The application of such films is restricted to areas in which heat transfer is not a key operational factor.

Cathodic protection is done to reduce galvanic attack by placing sacrificial anodes. Design and placement of these anodes is considered a science in itself. When properly installed they can reduce the loss of steel from the tube sheet of heat exchangers employing copper tubes, for example. Sacrificial anodes have been successfully used to supplement chemical programs in several cooling systems. One downside of cathodic protection is that it is only limited to galvanic corrosion and it cannot help with other types of corrosion such as under-deposit corrosion or microbially induced corrosion.

Corrosion Inhibitors.

As noted earlier, the corrosion process involves an anodic and a cathodic reaction. Therefore in theory, any ***chemical*** applied to the water to stop the anodic reaction will stop corrosion. Under the same assumption, any ***material*** added to reduce the rate determining cathodic reaction will reduce corrosion.

From these concepts corrosion inhibitors can be characterized as ***anodic, cathodic,*** or ***both anodic and cathodic.*** Some examples of anodic inhibitors include *chromate, orthophosphate, nitrite, and silicate*; cathodic inhibitors include *calcium carbonate, polyphosphonate, and zinc;*

and some of the inhibitors that are considered both anodic and cathodic include *organic filming amines, and phosphonates.*

Of the anodic inhibitors, chromate was once the most widely used. It provided a hard film of reduced chromate and alpha iron on the surface of the metal. Unfortunately, chromates are highly toxic and its use has been prohibited in most countries. If anodic inhibitors are not applied in proper quantities they do not provide proper *passivation* to all anodic sites. Under these conditions these few anodic sites become the focal point of the corrosion process and deep pitting can result.

Cathodic inhibitors generally *reduce* the corrosion rate by forming a barrier or film at the cathode, restricting the hydrogen ion or oxygen migration to the cathodic surface to complete the corrosion reaction. The cathodic inhibitors are all considered *safe* compared to the risks of anodic inhibitors used alone.

Other approaches.

The first step in correcting or controlling the corrosion potential of a water distribution system should be to establish the most beneficial conditions under which corrosion is reduced to its minimum. In many cases the corrosion can be brought under control by carrying a positive Langelier index or a stability index below 6. In low hardness-alkalinity water with a high corrosion potential, Lime or a combination of caustic soda-calcium chloride can be added to increase the calcium and alkalinity of the water.

Dispersants, while not corrosion inhibitors per se, play a prominent role in controlling corrosion by preventing solids deposition and subsequent formation of oxygen concentration cells.

The Zeta Rod

Although not a corrosion inhibitor, the Zeta Rod allows a cooling system to operate under conditions in which the corrosion potential is minimized. By running at high cycles, precipitation of carbonates occurs. This effect is similar to the addition of lime mentioned above. At high cycles of concentration, the pH of the water solution will be such that it will provide a positive Langelier index. In addition to these effects, the Zeta Rod acts as a superior dispersant which prevents the formation of deposits, both mineral and organic, on the metal surfaces. And last, the electrostatic field generated by the Zeta Rod causes an electrolytic migration of cations towards the metal surfaces. This enhanced double layer prevents oxygen or hydroxyl ions from reaching the metal to complete the corrosion process.

Corrosion Testing: Plant Tests.

Test Coupons. When conducting plant testing it is necessary to install the coupons in such a manner that they will not come into contact with other metals and alloys; this avoids having their normal behavior disturbed by galvanic effects. It is also desirable to protect the coupons from possible mechanical damage. The coupons should preferably have a large surface-to-mass ratio.

Corrosion rates may vary during testing. Since the rate obtained from coupon testing is averaged over time, the frequency of sampling is important. Generally, measurements made over longer times are more valid. Coupon monitoring is most useful in environments where corrosion rates do not significantly change over long time periods. Since corrosive conditions can change significantly from one location to another, coupon data is best used for relative comparisons and to obtain an approximate corrosion rate at a particular point in the system rather than to precisely calculate the corrosion rate.

Short-time tests can give misleading results on alloys that form ***passive films***. The phenomenon of forming a protective film is observed with many materials, and therefore short tests on such materials would indicate high corrosion rates and would be completely misleading. Depth of localized corrosion should be reported for the actual test period and not interpolated or extrapolated to an annual rate. A second reason to perform long-term tests is the potential for error as a result of the cleaning operation. Coupon cleaning procedures are designed to remove all of the deposits without disturbing the remaining uncorroded metal of the coupon. However, it is not uncommon for a small amount of the underlying metal to be removed along with the deposits.

Precautions to take when starting a Zeta Rod program.

As it has been mentioned above, the Zeta Rod is not a corrosion inhibitor per se, however, it allows cooling systems to operate under conditions such that the corrosion potential is minimized. Corrosion rates observed in Zeta treated systems are equal or better than those observed under conventional chemical programs.

It is important to keep in mind that the Zeta Rod has been proven to remove deposits from the fill of cooling towers and other surfaces. Sometimes this deposit removal can be very aggressive, and in other cases it can be slow and hard to notice. When the removal of old deposits takes place in a rapid manner, certain precautions should be taken so that the monitoring of the corrosion rates are not skewed by some of these effects.

When old deposits are removed from the surfaces small particles may be reintroduced into the water flow. The suspended particles will almost certainly adhere to the freshly exposed surface of the coupons. This is especially true of the mild steel coupons. These deposits will generate oxygen concentration cells which will make the coupons show greatly accelerated corrosion rates, typically in the form of pitting, that are not representative of the actual conditions throughout the system. In order to prevent this from occurring it is recommended to put a fine strainer upstream from the corrosion coupons to prevent these particles from forming deposits on the coupons.