Corrosion and Soft Water

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CORROSION

The metals used in plumbing systems are rarely found in nature in forms that are directly useful, by humans. Instead, they exist as ores, stable mineral compounds with chemical and physical properties quite different from those of the pure metals. To make these minerals useful, they must be processed using the electrochemical methods to reduce the ores to elemental metals.

This reduction of ores is necessary because elemental plumbing metals are not inherently stable. With time and exposure to the natural environment, the elemental metals are converted to the more stable mineral compounds. This action - corrosion - changes the chemical and physical properties of the metals, frequently destroys the usefulness of a metallic article or structure, and is a completely natural process.

Thus, corrosion has been defined as the natural reversion of a metal to an ore.

CORROSION CHEMISTRY

Although the corrosion chemistry of each metal differs in details, the general principles apply to most of the commonly used metals. Thus, the reactions of iron in the following examples illustrate these basic principles.

Water is widely recognized as a solvent for virtually all materials. When water and iron are in contact, a few molecules of iron go into solution with a reaction which leaves a few electrons behind in the mass of metal. If no other factors are involved, however, this reaction would stop, for the charge of electrons developed in the metal would inhibit further reaction. The loss of metal into the water can be discharged.

Free hydrogen ions found in all water, to at least some extent, provide a means of removing the excess electrons from the mass of metal. The electrons and the hydrogen ions react to first form atomic hydrogen, and then molecular hydrogen gas. As the hydrogen forms, it too tends to inhibit further corrosion by forming a very thin gaseous film at the surface of the metal. This "polarizing" film can be effective in reducing water to metal contact and, thus, in reducing corrosion. Yet, it is clear that anything which breaks down this barrier film tends to increase the rate of corrosion.

Dissolved oxygen in the water will react with the hydrogen, converting it to water, and destroying the film. High water velocities tend to sweep the film away, exposing fresh metal to the water. Similarly, solid particles in the water can brush the hydrogen film from the metal.

Other corrosion accelerating forces include high concentration of free hydrogen ions (acid water) which speed the release of the electrons, and high water temperatures that increase virtually all chemical reaction rates. Thus, a variety of natural and environmental factors can have significant effects on the corrosion rate of iron, even when no other metals or special conditions are involved.

ELECTROLYTIC CELLS

It is rare that a plumbing system contains nothing but simple, pure iron. Electrolytic cells of various types are common in most systems.

The galvanic cell, set up when dissimilar metals are in contact with each other and with conductive water, generates electricity. The flow of electrons created by such a cell accelerates the corrosion of iron in contact with copper or brass, for example, by stimulating the flow of electrons away from the iron.

Clearly, it is difficult to eliminate all dissimilar metals in a plumbing system. Yet, even if this were possible, minor impurities in the iron could create galvanic cells. Such impurities are present in all commercial grades of plumbing materials, for they are difficult to remove at reasonable costs.

Differential aeration cells, created when the dissolved oxygen concentration varies between adjacent areas on iron, have similar reactions and effects. Such conditions can develop under scale or rust, at rivets, joints or crevices, or under deposits of organic matter such as slimes or iron bacteria. Thus, a partially coated surface may actually accelerate this type of corrosion.

In some circumstances, even temperature or stress variations between adjacent sections of a common metal can create electrolytic cells. Stray electric currents, sometimes caused by breakdowns of electrical systems grounded to plumbing, can cause major corrosion where the current leaves the pipe and a special form of electrolytic cell is created.

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CORROSION ACCELERATORS

As indicated above, at least some corrosion will occur whenever a metal is exposed to water, and a number of factors will accelerate corrosion. These include:

1. **Low pH** – Acid waters clearly accelerate corrosion by providing a plentiful supply of hydrogen ions. Although even absolutely pure water contains some free hydrogen ions, free carbon dioxide in the water can multiply the hydrogen ion concentration many times. When carbon dioxide dissolves in water, it reacts with the water to form carbonic acid, a so-called weak acid, but an effective source of acidity. Even more acidity is sometimes encountered in acid mine waters, or in those contaminated with industrial wastes.

2. **Dissolved oxygen** – This gas works to destroy the protective hydrogen film and to oxidize dissolved iron to an insoluble form. Deposits of rust in a plumbing system can form differential aeration cells and accelerate corrosion.

3. **High mineral concentrations** – The electrical conductivity of water increases with its dissolved mineral concentration. Thus, highly mineralized waters readily conduct the electrical currents of electrolytic cells and accelerate this type of corrosion.

4. **Water temperatures** – High water temperatures not only accelerate the chemical reaction of corrosion, but also may reverse normally protective systems. For example, zinc galvanizing protects iron or steel at normal temperatures by "plating" a protective deposit over exposed iron at a pit or break in the zinc coating. However, at temperatures above 160° F., the iron will attempt to deposit on the zinc, thus creating a deep pit or hole where the iron is exposed.

5. Other physical factors, including high flow velocities; solid particles in the water, and deposits on metal surfaces may cause or accelerate corrosion.

CORROSION IN HARD AND SOFT WATER

From the above, it is clear why many natural waters have strong corrosive activities. In sections of New England and the far Northwest, much of the underground strata is granite which has very low solubility, does not neutralize natural carbon dioxide concentration, and has little on dissolved oxygen. Thus, groundwaters in these areas are corrosive because of the acidity due to carbon dioxide and the dissolved oxygen present.

Sections of the southeastern states, where much of the underground structure is organic matter, have waters, which are low in minerals and oxygen, but high in carbonic acid derived from decaying organic matter. The corrosive nature of these low hardness waters is well established.

At the other end of the range are many waters found in the Southwest, where extremely high hardness and mineral concentrations are common. Although usually alkaline in nature, these waters have high electrical conductivities, and in arid regions, may have high dissolved oxygen concentrations. Thus, these highly mineralized waters are known to be extremely corrosive, but for different reasons than the naturally soft, acid waters.

The lowest rates of corrosion are usually found with well waters of moderate mineral concentrations in limestone regions. Such waters have little dissolved oxygen, and the natural carbon dioxide has been largely neutralized by the alkalinity dissolved from the underground minerals. The conductivity is relatively low, so galvanic corrosion is not serious under usual circumstances. This water is found in wells over most of the Midwest.

Surface water supplies frequently follow the trends of water quality of groundwaters in a region, but usually have lower mineral concentrations because of the dilution effects of rain and snow. However, surface waters are almost always saturated with dissolved oxygen from the air, and this element often produces serious corrosion.

Thus, it is evident that all water is corrosive to the metals in plumbing systems to at least some degree, and that both naturally soft and naturally very hard waters can produce high corrosion rates.

CORROSION IN SOFTENED WATER

The removal of hardness with an ion exchange water softener does not affect the factors which cause or accelerate corrosion. Softening does not change the pH or carbon dioxide concentration, the dissolved oxygen concentration, or the total chemical concentration of minerals. A softener may reduce the amounts of solid particles in the water, but obviously cannot change other physical factors such as temperature, flow rates through pipes, or volumes of water used. Thus, ion exchange softening neither causes nor controls corrosion.

Unfortunately, certain methods of calculating the probable corrosive potential of natural waters have been misapplied to softened waters, with misleading results. The Langelier Index, and some of its modifications, may be used to indicate whether or not particular water will precipitate calcium carbonate scale at a given temperature. This information certainly is useful to those responsible for operating many systems.

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Further, when applied to natural waters, these methods of calculation may indicate that when such an excess of carbon dioxide over alkalinity exists in the water, the precipitation of calcium carbonate would be impossible. Such excesses of carbon dioxide clearly make waters strongly corrosive, as demonstrated by the low pH waters found in New England and the Northwest.

These methods, however, should not be applied to water softened by ion exchange since there is no real chemical similarity with the naturally soft acid water. The removal of calcium by a softener obviously prevents scale formation. Yet, as indicated above, it does not change either the carbon dioxide content of the water or the natural alkalinity which tends to neutralize the carbon dioxide. Thus, softening will not make a water more acid or affect the other corrosion accelerating factors.

Some persons argue that the precipitation of calcium carbonate scale will protect the metals from corrosion. While some scales are capable of such protection, other scales are porous or soft, and thus, nonprotective. Further, it is rare that scale formation is uniform, for the heaviest scale usually forms at points of heat transfer and at low points in a system. In a water heater, for example, most scale forms at the bottom where heat is applied, while the top of the heater tank may show little or no scale. Thus, even in hard, scale-forming waters, thousands of water heaters fail every year due to corrosion. Examinations of these heaters usually show that corrosion has occurred under or through the scale or in locations where protective scale has not formed. Thus, it is clear that corrosion protection is not assured simply because a water will precipitate calcium carbonate, as indicated by various calculations or test methods. Further, none of these methods take into account the effects of dissolved oxygen, water flow velocities, the presence or absence of solid particles, the volume of water through the system, or other environmental factors which affect the rate of corrosion.

As stated by Schneider and Stumm of Harvard University; [1]

"It is a commonly accepted belief that the corrosive behavior of a natural water is influenced predominantly by pH and calcium carbonate saturation (frequently expressed by the Langelier Saturation Index). The results of extensive studies involving both field and laboratory investigations indicate that this concept presents an oversimplified picture of the problem. As corrosion in natural waters depends on so many interdependent variables, no simple equation or index is capable of describing adequately the corrosive potential of a water, and no generally applicable recipe for appropriate corrective treatment can be given."

CORROSION CONTROL PROCEDURES

When corrosion does occur in a water supply, several corrective treatments are useful in reducing the corrosion rate. Clearly, the best method is to prevent water to metal contact, and a number of coating and plating procedures are used for this purpose. Yet, these methods are not always possible or economically feasible, and a number of chemical treatments have been developed to condition the water to reduce the corrosion rates to reasonable levels.

In industrial systems or where the water will not be used for human consumption, oxygen scavengers are frequently used to reduce this corrosive gas in the water. High concentrations of "passivating" chemicals are common in reticulating systems because of the inhibiting effects. Yet, neither of these approaches are applied to water used in households because of the possible toxic effects of the chemicals, and because some make the water unsuitable for general household use producing heavy stains or discolorations.

Thus, corrosion control methods for municipal and household water systems are currently limited to two approaches; neutralization of acidity with alkaline materials, and the feeding of small amounts of chemicals, which tend to line the water system with protective films.

Calcite (calcium carbonate) and magnesia (magnesium oxide) filters have long been used to neutralize household acid waters. As water flows through beds of these minerals, the acidity dissolves enough of the filter media to produce essentially neutral water. Other installations use chemical solution feeders to introduce solutions of soda ash (sodium carbonate) or caustic soda (sodium hydroxide) to the water in proportion to the acidity, producing a neutral or slightly alkaline water. Some municipal systems use lime (calcium hydroxide) to increase alkalinity and pH. Several types of polyphosphates and silicates may be fed into water systems for corrosion control. In some cases, slowly soluble forms are fed with "pot"-type feeders, while in others solutions are fed with chemical solution pumps. Both the silicates and polyphosphates tend to form thin films on the interior surfaces of the plumbing, thus reducing the water to metal contact. Feeds should be essentially continuous, however, to form and maintain the protective films.

References:
[1] *Schneider, Carl R. and Stumm, Werner: "Evaluation of Corrosion in Distribution Systems." Journal AWWA May 1964, pp. 621-631.*

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