Understanding Corrosion

Corrosion, resulting in the severe degradation of materials, is one of the most expensive engineering problems in our industrial society; estimates have been made that the annual cost of corrosion in the United States exceeds $100 billion.

Welded structures are often subjected to corroding environments. In some cases, the weld and base metal corrode uniformly at the same rate; in other cases, the results are accelerated corrosion of the weld compared to the base metal, or the base metal may corrode at a much faster rate leaving the weld metal relatively intact. Welding, and its associated heat input, can also contribute to other corrosion problems.

Corrosion has been defined as “the destruction of a metal by chemical or electrochemical reactions with its environment.” (Definitions used are those developed by Dr. Mars Fontana and/or NACE.) In today’s world of ever-increasing materials available to the designer, this definition must be expanded to cover other materials in addition to metals since environmental failures of non-metallics also occur. However, since our primary interest is in weld corrosion of metals, this discussion will be limited to metals only.

Several general statements can be made regarding metal corrosion:
- Corrosion of metals always occurs at the anode (oxidation), with the cathode (reduction) being protected.
- There is electron flow between the anode and cathode during corrosion.
- Nascent, or atomic, hydrogen (H+) is always formed at the cathode during corrosion.

Following are descriptions of the eight primary forms of corrosion.

General Corrosion

The most common form of corrosion is general corrosion, also called uniform attack, which is defined as “a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface, or over a large percentage of the exposed surface.” During this type of corrosion, the material corrodes quite evenly over its surface, or the majority of its surface, that is exposed to the corroding environment — Fig. 1.

Generally, when carbon steels corrode uniformly and corrosion scales form, the thickness of the scale can be about 7 to 10 times as thick as the original metal thickness consumed to form the scale. Thus, a 1/4-in. steel plate completely corroded can form a scale of 1.5 to 2 in. or more. Aluminum alloys also can form thick scales in some exposures, and this scale formation has been termed “blooming.” These aluminum scales are quite loose, almost fluffy in nature, are very unprotective, and can be easily removed with a little light mechanical scraping.

Examples: copper in a weak nitric acid solution will dissolve; steel immersed in seawater eventually becomes entirely consumed; aluminum in a caustic solution will dissolve; water pipes in houses become quite thin and fail.

The rate of general corrosion is usually described in terms of the thickness lost per unit time. In the United States, a common term is mils per year (mpy). A mil is 0.001 in., and an acceptable corrosion rate for steel used in common applications such as storage tanks or petrochemical equipment is usually 10 mpy or less.

Avoiding General Corrosion

To protect against general corrosion, the most obvious solution is to avoid contact between the metal and the corroding environment. If you eliminate the corrosive environment from contact with the metal, no corrosion occurs. Often this is impractical, so other methods had to be developed.

One approach is to add a “corrosion allowance.” In practice, this means making the item thicker than that required by the engineering design. Instead of using 1/4-in. steel plate when the known general thickness rate is 10 mpy, select a 3/8-in-thick plate. The extra 3/8 in. of steel thickness will withstand an additional six years of service if corrosion occurs on both sides; twelve years if corrosion only occurs on one side.

Another common method is to apply a protective coating to the metal surface to exclude the corroding environment; a coat of paint properly applied will provide excellent protection for an extended period of time. Zinc coatings, also called galvanizing, are often applied to steel to improve resistance to atmospheric exposure.

Other methods for controlling general corrosion include lining the metal that will corrode with a protective one, adding corrosion inhibitors to the corroding environment, anodic or cathodic protection of the component, or upgrading to other metals having better corrosion resistance.

General corrosion usually results in a long-term condition prior to failure, and its avoidance is usually straightforward. It does, however, constitute a major portion of the economic loss suffered by industry, and its detriment cannot be minimized.

Pitting Corrosion

Fig. 2 — Interior pipe wall of carbon steel boiler feed waterline showing severe oxygen pitting due to poor water quality control. Note rusty pit at arrow showing complete perforation of pipe wall.

Pitting corrosion is defined as “extremely localized corrosion, resulting eventually in holes in the metal.” The total area based on the pits’ diameters is usually quite small compared to the total exposed surface area of the component — Fig. 2. For example, the majority of a

Intergranular Corrosion

may occur quickly due to perforation. Compared to general corrosion, yet failure regarding pitting since often only minor measurement method has little value ensuring pit depth vs. time; the normal mpy of pitting rates is usually done by measuring, and others. Measurement factors such as the alloy type, surface the nature of pitting depends on many pressure-containing shell. A single pit that extends entirely through home hot water heater may be in good condition, but the heater may leak due to a single pit that extends entirely through the pressure-containing shell.

Pitting mechanisms are often quite complex. Considerable research has been done in trying to understand the pitting mechanism and its avoidance. The nature of pitting depends on many factors such as the alloy type, surface condition of the metal, exposure environment, temperature and concentration of the corroder, and others. Measurement of pitting rates is usually done by measuring pit depth vs. time; the normal mpy measurement method has little value regarding pitting since often only minor weight loss occurs from pitting compared to general corrosion, yet failure may occur quickly due to perforation.

Avoiding Pitting Damage

Protective coatings are very effective against pitting damage provided they are completely continuous over the entire surface and contain no breaks. Often, if the coating contains scratches or breaks, pitting not only occurs, it does so at a much higher rate than if there were no coating at all. The increased pitting rate is due to the relatively small area of metal actually exposed to the pitting agent's inherent driving force; most of the area is protected, but a very small area is subject to more severe pitting.

Alloy upgrades are another common solution. For example, if carbon steel is failing by pitting in water services, a switch to a copper-based alloy may solve the problem. Electrochemical protection methods are also effective in reducing or eliminating pitting damage, and corrosion inhibitors may reduce the pitting attack.

Intergranular Corrosion

This form of corrosion is defined as “localized attack at, and adjacent to grain boundaries, with relatively little corrosion of the grains.” Metal structures are composed of very small grains, or crystals, with a particular structure, and arranged in random patterns separated by grain boundaries. The individual grains grow during solidification of the metal, and where two grains come together at different orientations, the line or irregular plane of contact is called the grain boundary.

Often, intergranular corrosion, or intergranular attack (IGA), is due to the lack of proper heat treatment of the base metal. Welding that is not followed by postweld heat treatment is often the root cause of IGA since the heat of welding reduces the corrosion resistance of the metal by affecting its original heat treat-

Avoiding Intergranular Attack

The most obvious method to avoid IGA based on the above is to not expose the 300 series to corroding environments except when they are in the SAWQ condition. A common example of IGA is the result of welding 304 stainless steel without subsequent postweld heat treatment, and then exposing it to severe environments such as hot, concentrated nitric acid.

Many alloys are subject to IGA when exposed to a variety of environments but IGA of the 300 series stainless steels is one of the most common occurrences — Fig. 3. To aid in our understanding of how welding affects the 300 series stainless steels, we must understand “sensitization,” the term given to the phenomenon of precipitation of chromium carbides at grain boundaries, a precursor to selective grain boundary corrosion. The 300 series stainless steels are primarily alloys of chromium, nickel, and iron, with minor amounts of carbon. Most standard grades in the 300 series have a carbon content maximum of 0.08%. To maximize these alloys’ corrosion resistance, they are given a “solution anneal, water quench” heat treatment (SAWQ), which takes the alloying elements into solid solution. After such a heat treatment, welding can cause sensitization by exposing portions of the metal to the sensitizing temperature range of 800°–1650°F. In fact, welding causes the base metal to be exposed to this temperature range twice; once on heating and again on cooling back to room temperature. Thus, welding on the 300 series alloys usually results in some degree of sensitization, from minor to severe, depending on the rate of cooling, which can be affected by the welding process, base metal thickness, electrode size, etc. Because of this sensitization problem, the 300 series alloys are seldom preheated when fabricating for corrosive service since this only increases the time of exposure to the sensitizing conditions.

Avoiding Selective Leaching

Selective leaching is defined as “the removal of one element of a solid solution alloy by corrosion.” An early type of selective leaching corrosion of brass alloys was named “dezincification.” Brass is an alloy made primarily of copper and zinc. If the zinc was preferentially removed from the alloy by corrosion, it was termed “dezincification.” However, the description “selective leaching (of the element being removed)” is the preferred approach.

During selective leaching, one element is removed, often leaving a residue or spongy matrix of the remaining elements having reduced mechanical strength.

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Avoiding Selective Leaching

The primary approach is to avoid exposing alloys to environments that cause selective leaching. Study of selected alloy families will usually result in noting specific environments to avoid. Also, additional elements such as arsenic or
antimony can be added to the copper alloys to reduce selective leaching.

The occurrence of selective leaching is quite minimal today because of our increased understanding of the mechanism, the addition of elements to reduce the problem, and the avoidance of exposure combinations leading to this form of corrosion.

**Stress Corrosion Cracking**

![Fig. 4 — Section of 316 stainless steel piping showing severe SCC from external chlorides.](image)

Defined as “cracking caused by the simultaneous presence of stress, oxygen, and a corrosive medium,” this phenomenon is one of the more difficult and costly corrosion types to avoid. Early stress corrosion cracking (SCC) failures were little understood and often had catastrophic results. SCC is often associated with little or no general corrosion damage as well as dramatic failures in unexpected circumstances.

Today, we have discovered many combinations of metals and environments that are particularly susceptible to SCC. Metals can crack in environments of caustics, chlorides, cyanides, ammonia, sulfates, and hydrogen sulfide, to name a few — Fig. 4.

With SCC, stress is a primary requirement for the cracking mechanism. Stress can be induced into a component by several sources: applied stress during the service application; residual stress from cold working (drawing, forming) during manufacture; residual stress from welding; or a combination of stresses from multiple sources. The amount of stress required to promote SCC is often referred to as the “threshold stress”; for many alloys, the threshold stress range is 2000–15,000 lb/in.². Below this threshold, SCC is unlikely to occur. Other factors necessary for SCC are the necessary chemistry, moisture, and oxygen or an oxidizing agent.

**Avoiding Stress Corrosion Cracking**

During welding, the residual stress levels can often be equivalent to the yield strength values for the metals being welded. An obvious solution for reducing residual stress from welding, and the susceptibility to SCC, is to stress relieve the welded component to reduce its residual stress level below the threshold stress level required for SCC. This works well for carbon and low-alloy steels. For service in SCC environments such as caustics and cyanides, carbon and low-alloy steel welded components or piping cold bends are often stress relieved at temperatures of 1100°F–1300°F. An alternate stress relief method is to normalize the components at 1650°F–1750°F for several minutes followed by still-air cooling.

Stress relief is usually not the proper approach for austenitic materials such as SS 304 or 316 in chloride environments. These alloys suffer sensitization when held in the 800°F–1650°F range and the typical stress relieving sequence for these alloys (1650°F, slow cool) will reduce their residual stress but usually leaves the materials severely sensitized, thereby lowering their general corrosion resistance.

The usual solution for avoiding SCC in austenitic materials is to substitute alloys resistant to chloride SCC. This is accomplished by selecting those alloys having a much higher nickel content. Avoiding SCC for austenitic stainless steel grades requires increasing the nickel content to 30% or even higher depending on the severity of the environment.

**Erosion/Corrosion**

![Fig. 5 — Erosion/corrosion damage in piping due to severe turbulence of process fluid caused by welding Schedule 40 pipe to a thicker Schedule 80 elbow resulting in an abrupt change in inside diameter.](image)

Defined as “the increase in corrosion rate due to the relative motion between the corrosive fluid and the metal surface,” this corrosion type is often found in pumping and piping systems and any case where a fluid flows across or impinges onto a metal surface — Fig. 5. The increase in corrosion rate caused by the fluid motion can be minor or catastrophic. Corrosion often occurs, for example, in tubular heat exchangers due to high fluid velocities. Often there is a “threshold velocity” of the fluid and metal combination below which corrosion rate increases do not occur. Corrosion testing will aid in determining what fluid velocities must be avoided for particular combinations of fluids and alloys.

**Avoid Erosion/Corrosion**

If erosion/corrosion is a potential problem for a proposed piping system, it becomes imperative that complete joint penetration, without excess, is the goal. Welder training and proper inspection techniques such as radiography will aid in reaching the goal of long service life. Alternate methods of achieving a smooth inside diameter at the weld joints include modifying weld joint geometry and the use of consumable inserts. The fluid velocity can also be kept below the threshold velocity value by increasing the piping diameter. Turbulence and impingement can also be avoided in other types of equipment through design considerations such as impingement baffles or alloy upgrades.

**Crevice Corrosion**

![Fig. 6 — Back side of a carbon steel tube sheet of a shell and tube heat exchanger showing crevice corrosion of tubesheet at tubesheet hole.](image)

Defined as “intense, localized corrosion within crevices, usually associated with small volumes of stagnant solution,” this corrosion type can be quite prevalent in flanged and bolted piping systems — Fig. 6. An alternate term often used for this type of corrosion is “concentration cell” corrosion; this concentration cell form may also be considered a separate type of corrosion. Key words in the definition are “stagnant solution.” Consider a circulating fluid contained within piping and equipment: the majority of the equipment is exposed to free-flowing liquid while flanged joints often...
contain the solution in a stagnant, quiescent condition. The presence of both flowing and stagnant fluids within a system can lead to differences of ion concentrations within the liquid. Areas beneath the flange or gasket often contain different concentrations of metal ions or oxygen than the open surfaces. These differences can lead to selective corrosion adjacent to or beneath the crevice formed. Additionally, surface scales or surface debris on metals can also create concentration cells leading to crevice corrosion. Crevice corrosion can also occur when metals are in direct contact creating a tight crevice between them.

Avoiding Crevice Corrosion

With the great number of crevices formed in manufacturing and assembling complex equipment, and the likelihood of metal surface scales or debris forming, the normal solution for crevice corrosion is to select alloys not subject to damage in the particular services. Efforts to avoid crevice corrosion by selecting “nonwicking” (nonabsorbent) gaskets have been successful in some cases, but in others, crevice corrosion continued unabated. One of the primary advantages of welded piping joints over flanged systems is to eliminate crevices at the joints. Again, it is imperative that weld quality is sufficient to totally eliminate the crevice; incomplete joint penetration and incomplete fusion of the root joint must be eliminated for this approach to be successful.

Galvanic Corrosion

Galvanic corrosion is defined by the statement “a potential (voltage) difference exists between two dissimilar metals when they are immersed in a corrosive or conductive solution; this permits electron flow and corrosion of the less resistant metal” — Fig. 7.

There has been considerable discussion of galvanic effects regarding corrosion; the most often cited anode/cathode combinations in saltwater are usually listed showing which alloys are anodic to others.

Galvanic corrosion, as a primary mode of failure, is actually quite rare in most industrial environments. Numerous piping systems use combinations of carbon steel piping connected to stainless valves selected for erosion/corrosion resistance and do not suffer galvanic corrosion problems. Many other dissimilar metal combinations are likewise used with little or no galvanic corrosion.

We can use these galvanic differences to protect steel structures. Many offshore oil platforms made from carbon steel have large “anodes” of zinc or zinc alloys attached to them to protect the steel. The zinc anodes preferentially corrode, thereby protecting the steel from corrosion. As the zinc anodes disappear over time, they must be replaced on some frequency to maintain protection. The number and location of the anodes must be carefully thought out to provide complete protection. The “throwing power” of zinc and its alloys refers to the area of steel one anode will protect, and it can be considerable depending on several factors such as alloy content, size, temperature, and water quality.

Avoiding Galvanic Corrosion

Generally, little is needed to avoid galvanic corrosion for most industrial applications since it seldom occurs. However, some industries must take careful precautions in selecting metal combinations to avoid problems. The most common solutions to galvanic corrosion are the selection of alloys that exhibit similar potentials for the anticipated service, or the use of nonmetals as one of the material couples. Another technique used with limited success is the electrical isolation of the alloy combination to eliminate electron flow between the two metals. ◆

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