anodes. Anode and cathode areas may shift from time to time as the corrosion process proceeds, resulting in essentially uniform corrosion.

Reactions at the cathode surface most often control the rate of corrosion. Depending upon the nature of the electrolyte, the hydrogen generated at the cathode surface may:

1. Accumulate, so as to coat the surface and slow down the reaction. This process is called cathodic polarization.
2. Form bubbles and be swept away from the surface, thus allowing the reaction to proceed.
3. React with oxygen in the electrolyte to form water, or hydroxyl ion.

At the anode, the metal ion going into solution may react with a constituent in the electrolyte to form a corrosion product. With iron or steel, the ferrous ion may react with the hydroxyl ion in water to form ferrous hydroxide, and then with oxygen to produce ferric hydroxide (rust). These corrosion products may accumulate on the anode surface and slow down the reaction rate. This process is called *anodic polarization.*

ACCELERATING OR INTENSIFYING FACTORS

Moisture

As has been noted previously, an electrolyte must be present on a metal surface for corrosion to occur; no corrosion occurs in dry air. In most natural atmospheres, some moisture is usually present as water vapor, its amount being expressed as *percent relative humidity.* Vernon[9] demonstrated that, in pure air, practically no corrosion of iron occurs at relative humidities up to 99 percent. But, with contaminants present, such as sulfur dioxide or solid particles of charcoal, corrosion could proceed at relative humidities of 50 percent or above. Pure air is seldom encountered in practice. During rains, exposed metal surfaces are completely wetted, thus allowing the corrosion reaction to proceed as long as the metal remains wet.

The above conditions apply to iron and unalloyed steel. Many alloys may develop thin corrosion product films or oxide coatings so as to remain essentially unaffected by moisture.

Oxygen

With electrolytes consisting of water solutions of salts or acids, the presence of oxygen in the media tends to accelerate the corrosion rate of ferrous metals by depolarizing the cathodic areas through reaction with hydrogen generated at the cathode, and thus allowing the anodic reaction to proceed. In many ferrous systems employed for handling water, such as boiler systems or hot water heating systems, oxygen is removed to reduce the corrosion rate. Examples are: the addition of oxygen scavenging chemicals, such as sulfites, to the system, or the use of deaeration equipment to expel the dissolved oxygen.

Presence of oxygen in the media does not affect all alloys in the manner described above. With alloys which develop protective oxide films, such as stainless steels, oxygen may reduce corrosion by maintaining the oxide film. The media, free of oxygen, might be capable of causing some corrosion of the alloy, but with oxygen present, the oxide film becomes reinforced and thus precludes corrosion.

Solutes

With ferrous materials such as iron and steel, mineral acids tend to accelerate the corrosion rate, whereas alkalies tend to reduce it. Since the corrosion reaction at the cathode is related to the relative concentration of hydrogen ions present, the higher the concentration (the more acid the media), the less likely will the cathode area become polarized. Alkaline solutions, containing a much higher concentration of hydroxyl ions present than hydrogen, promote polarization of the cathode areas, thus reducing the rate of dissolution at the anode. Relative acidity or alkalinity of a solution is defined as *pH*, with a neutral solution having a *pH* of 7. Solutions increase in acidity as the *pH* decreases, and increase in alkalinity as *pH* increases.

The corrosivity of most salt solutions will depend upon whether they tend to be neutral, acid, or alkaline when dissolved in water. As an example, aluminum sulfate is the salt of a strong acid (sulfuric acid), and a weak alkali (aluminum hydroxide). When dissolved in water a solution of aluminum sulfate is acid in nature and tends to act towards iron as would a dilute acid.

Since alkaline solutions are generally less corrosive to ferrous systems, it is practical, in many closed water systems, to minimize corrosion by the addition of an alkali or alkaline salt, to raise the *pH* to 9 or higher.

Differential Solute Concentration

As noted previously, a potential difference between anode and cathode areas is necessary for the corrosion reaction to proceed. Such a potential difference can be established at different locations on a metal surface due to differences in concentration of a solute in the media at these locations. Corrosion caused by such circumstances is commonly called *concentration cell corrosion.* Such cells may be of two general types, metal ion concentration cells and oxygen concentration cells.

In the metal ion cell, the metal surface in contact with the higher concentration of dissolved metal ion becomes the cathodic area, and the surface in contact with the lower concentration the anode. The metal ions involved may be a constituent of the media, or may result from the corroding surface itself. The differences in concentration in the media may be caused by flow of the media sweeping away the dissolved metal ions at one location and not at another. Such differences could occur at crevices, or due to deposits of one sort or another. The anodic area is to be found outside the crevice or deposit, where the metal ion concentration is least.

In the oxygen concentration cell, the surface area in contact with the media of higher oxygen concentration becomes the cathodic area, and the surface in contact with the media of lower oxygen concentration becomes the anode. Again, the existence of crevices or foreign deposits on the metal surface may produce conditions favorable to corrosion through this mechanism. The anodic area, where corrosion proceeds, will be in the crevice or under the deposit.

Galvanic or Dissimilar Metal Corrosion

Another factor which accelerates the corrosion process may be differences in potential of dissimilar metals coupled together and immersed in an electrolyte. Many factors control the severity of corrosion resulting from such dissimilar metal coupling:

1. The relative differences in position (potential) in the galvanic series, with reference to a standard electrode. The greater the difference, the greater is the driving force of the reaction. The galvanic series for metals in sea water is shown in Table 1.
2. The relative area relationship between anode and cathode areas. Since the amount of current flow, and therefore, total metal loss, is determined by the potential difference and resistance of the circuits, a small anodic area will corrode more rapidly, that is, it will be penetrated at a greater rate than a large anodic area.
3. Polarization of either the cathodic or anodic area may reduce the potential difference, and thus reduce the rate of attack of the anode.

In general, it is not wise to couple a small exposed area of a less noble metal with a large area of a more noble metal, in media where the less noble material may tend to corrode by itself. If such couples cannot be avoided, but one of the dissimilar metals can be painted or coated with a nonmetallic coating, the cathodic material should be so coated, rather than the anodic one. If the two materials can be insulated from each other, for example, by the use of an insulated joint in piping systems, the galvanic couple can be avoided. Where this is not possible, a *waster* heavy wall nipple section of the less noble material can be employed and can be readily replaced when it fails.

In piping systems handling natural waters, galvanic corrosion is not likely to extend more than 3 to 5 pipe diameters down the ID of the less noble pipe material.

In metal components exposed to the atmosphere, galvanic effects are likely to be confined to the area immediately adjacent to the joint.

Table 1 .... Galvanic Series of Metals and Alloys

Corroded End (anodic, or least noble)
Magnesium
Magnesium alloys
Zinc
Aluminum 2S
Cadmium
Aluminum 17ST
Steel or Iron
Cast Iron
Chromium-iron (active)
Ni-Resist
18-8 Chromium-nickel-iron (active)
18-8-3 Chromium-nickel-molybdenum-iron (active)
Lead-tin solders
Lead
Tin
Nickel (active)
Inconel (active)
Hastelloy C (active)
Brasses
Copper
Bronzes
Copper-nickel alloys
Monel
Silver solder
Nickel (passive)
Inconel (passive)
Chromium-iron (passive)
18-8 Chromium-nickel-iron (passive)
18-8-3 Chromium-nickel-molybdenum-iron (passive)
Hastelloy C (passive)
Silver
Graphite
Gold
Platinum
Protected End (cathodic, or most noble)

Stray Current Corrosion

Stray current corrosion is in essence merely one form of galvanic corrosion, the electrical potential driving the corrosion reaction coming from stray electrical currents from an electric generator. Such a phenomenon can occur on buried or submerged metallic structures. The soil or submergence media provide the electrolyte. The anode, or structure suffering accelerated corrosion, may be located some distance from the cathode structure. The most common source of stray currents are direct current electrical systems such as street railways, welding generators, and electroplating shop generators where electrical leaks to ground are difficult to prevent by insulation.

The corrosion attack by stray currents is usually restricted to the structure surface in contact with the soil or other submergence media.

More detailed information on this mechanism is given in Reference 6.

Effects of Stress

The presence of stresses in metallic structures rarely has significant effects on the uniform corrosion resistance of metals and alloys. There have been a few instances of stress accelerating corrosion with some materials, the more highly stressed areas usually being anodic to the less severely stressed areas. But such mechanisms are more commonly a laboratory curiosity than a practical reality.

On the other hand, stresses in specific metals and alloys can cause corrosion cracking when exposed to specific corrosive environments. The cracking is often catastrophic in its effects on the usefulness of the particular metal.

Almost all metals and alloys exhibit susceptibility to stress-corrosion cracking in one or more specific environments. The more common examples are steels in hot caustic solutions, high zinc content brasses in ammonia, and stainless steels in hot chlorides. For more details regarding specific materials, consult metal producers.

Stress-corrosion cracking can frequently be prevented by using the susceptible alloy in the annealed or stress-relieved condition, or by selection of a material known to be resistant to such attack by the specific media.

Temperature

There is a common misconception among some engineers that corrosion rates double for every 18 F deg rise in temperature. This idea comes from studies of chemical reaction rates where this ratio is a valid approximation. Such a ratio cannot necessarily be applied to corrosion reactions, and generalities as to the effect of temperature cannot be made.

In systems where the presence of oxygen in the media promotes corrosion, increase in temperature may increase corrosion rate up to a point. Oxygen solubility will decrease as temperature increases, and may approach zero at boiling in an open system. Therefore, the corrosion rate may decrease beyond a critical temperature level, due to a decrease in oxygen solubility. However, in a closed system, from which the oxygen cannot escape, the corrosion rate may continue to increase with temperature rise.

For those alloys which depend upon oxygen in the media for maintaining a protective oxide film, an increase in temperature and the corresponding reduction in oxygen content may greatly accelerate corrosion rate by preventing oxide film formation.

Temperature may affect corrosion behavior in yet another manner, by causing a dissolved salt in the media to precipitate on the surface as a scale, in which case the scale may tend to