

## Wet Corrosion

### *Conditions for Wet Corrosion*

Just as we live in an oxygen-rich environment, we also live in an environment that is often wet with rain, condensation, and, in many instances, sea water. Similar to their resistance to oxidation, polymers and ceramics are chemically stable in wet environments, but many metals corrode. The loss of metal by wet corrosion can be very rapid, even at low temperatures. By contrast, metal loss by oxidation is primarily a concern at high temperature because of the Arrhenius law temperature dependence, which is repeated here:

$$(\text{rate of reaction}) \sim e^{-Q/RT}.$$

$Q$  is an activation energy (J/mol),  $R$  is the universal ideal gas constant (8.314 J/mol·K), and  $T$  is the temperature in absolute degrees (K). Incidentally, engineers often prefer to express  $Q$  in units of joules per kilogram (J/kg), rather than joules per mole. In this case, the universal ideal gas constant  $R$  is not used but is replaced by a gas constant that depends on the molecular weight of the active chemical specie.

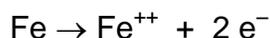
Electrochemical attack, the scientific name for wet corrosion, depends on three circumstances occurring simultaneously. This might seem restrictive, but the evidence of wet corrosion that we see all around us proves that these conditions are easily met. Rates of mass loss by wet corrosion may be thousands or even millions of times faster than rates of mass loss by oxidation.

1. There must be two dissimilar metals. Metals of different chemistry provide the obvious example, such as using steel nails to secure a copper sheet. Not as obvious is that, even with the same chemistry, differences in grain size or different amounts of cold working can drive electrochemical attack. This might occur in different regions of the same piece.
2. There must be an electrical connection between the dissimilar metals. Since metals are conductors of electricity, the most common occurrence is that the metals are touching each other.
3. Both dissimilar metals must be in contact with an aqueous (water) solution.

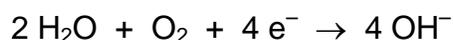
The result is that chemical reactions take place at each metal-liquid interface, with the interesting consequence that only one metal dissolves. The other metal is protected and undergoes no corrosion at all.

### *The Nature of Electrochemical Attack*

At the corroding metal, called the *anode*, metal atoms lose electrons and dissolve into the adjacent solution as ions. As an example, consider a piece of iron:



Because of the electrical connection, the electrons travel to the protected metal, called the *cathode*, where they take part in a variety of chemical reactions with molecules or ions in the liquid. The specific chemical reaction depends on the nature of the molecules or ions dissolved in the water. To continue our example, suppose that a portion of the iron previously considered is in contact with water containing dissolved oxygen. The cathode reaction in this case is:



Note especially that no metal is involved in this reaction. It occurs entirely within the liquid utilizing the electrons supplied by the anode reaction.

### *Prediction of Anode and Cathode*

Because there are many variables, often the wisest choice is to do experimental studies for the conditions of a specific engineering application. Here are some general observations.

<b>ANODE</b>	<b>CATHODE</b>
cold worked metal	annealed metal
grain boundaries	interior of grains
low O <sub>2</sub> concentration in solution	high O <sub>2</sub> concentration in solution

To predict the anode or cathode for different chemistries, two reference tables are available: the Standard Electrode Potential and the Galvanic Series in Sea Water. Each should be used with caution. They summarize controlled, standardized experiments, which may not closely match actual environments.

### *Prediction of Anode and Cathode – Standard Electrode Potential*

If two metals are suspended by electrically conducting wires into solutions containing ions of the metals, a voltage can be measured between the wires. If a mechanism for ion exchange between the liquids is included, we have an electrical battery. Common textbook examples include copper and zinc suspended in solutions of their respective sulfates, CuSO<sub>4</sub> and ZnSO<sub>4</sub>.

Only the voltage difference between two different metals can be measured. To standardize reference tables, zero volts is assigned to a *standard hydrogen electrode*, consisting of hydrogen gas ionizing at the surface of a platinum electrode. Now metals can be ranked by voltage, analogous to ranking oxide films by energies of formation. Under the standardized conditions of these measurements, the metal with the higher potential will be the protected cathode. The other metal will be the corroding anode. The following is an abbreviated sampling of some common metals.

Copper	$\text{Cu} \rightleftharpoons \text{Cu}^{++} + 2 \text{e}^{-}$	+0.34 volts
Tin	$\text{Sn} \rightleftharpoons \text{Sn}^{++} + 2 \text{e}^{-}$	-0.14 volts
Iron	$\text{Fe} \rightleftharpoons \text{Fe}^{++} + 2 \text{e}^{-}$	-0.41 volts
Zinc	$\text{Zn} \rightleftharpoons \text{Zn}^{++} + 2 \text{e}^{-}$	-0.76 volts

If iron nails are used to secure copper sheeting, the nails will corrode. If zinc is plated onto steel (galvanized metal), the zinc will be the anode dissolving into wet environments. However, if tin is plated onto steel (tinned cans), it is the steel that becomes the anode.

Chemists refer to the anode/cathode reactions as *redox* (reduction/oxidation) reactions. The following video expands our description using this language.

#### *Prediction of Anode and Cathode – Galvanic Series in Sea Water*

Sea water is often our corroding wet medium, and this series is a ranking similar to the voltages of the standard electrode potential. There are no numerical values assigned, but again, metals nearer one end of the ranking are observed to be cathodes relative to metals nearer to the other end of the table. One other difference from the standard electrode voltage ranking is that the galvanic series deals with specific engineering alloys, such as type 2024 aluminum and type 304 stainless steel.