

Corrosion text for proposed Revision of USCG NVIC 7-95

by Ed McClave

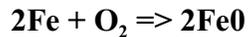
Part 1

Introduction to Corrosion Theory as Applied to Metal Parts of Wooden Hulls

A large proportion, probably a majority, of non-damage-related structural failures of wood hulls are caused by the failure, due to corrosion, of the metal fasteners that hold those wood hulls together. This section is an abbreviated presentation of the scientific principles of corrosion theory as it applies to the metal fasteners and underwater metal fittings of wood hulls. This discussion will cover the principles behind a number of corrosion processes - simple electrochemical corrosion, galvanic corrosion, stray-current corrosion, replacement or deposition corrosion, and also related methods used to protect metal from corrosion - sacrificial-anode cathodic protection and impressed-current cathodic protection, and the possible adverse affects on wood structures resulting from the application of cathodic protection.

Oxidation

Corrosion is the reversion of metals to the state in which they are typically found in nature, as oxides (the metal ores that are dug from the ground in mines are oxides). A typical chemical reaction for the corrosion of, for example, iron is:



Iron combines with oxygen to form iron oxide - which we call "rust" and which miners call "iron ore".

This chemical reaction is **direct oxidation** of the iron; it can also be termed **combustion**. When the reaction occurs, the chemical energy that was stored in the metallic iron during the refining process is recovered as heat. However, this reaction, and the direct oxidation of all of the metals we use in boat construction, requires an initial input of energy as heat to start the reaction, so direct oxidation occurs only at high temperatures. (This is the reaction when steel is cut with a cutting torch - the steel must first be preheated, then it burns readily when the oxygen is applied, eventually releasing more heat than was provided by the pre-heating).

Electrochemical Corrosion

Direct oxidation does not occur at room temperature. However, in the presence of water, there is an alternate path from metal and oxygen to metallic oxide called **electrochemical corrosion**, which does not require a large initial input of energy to get things started. The somewhat-more-complicated path from steel to rust that occurs in wet environments is this:

Step 1: $2\text{Fe} \Rightarrow 2\text{Fe}^{++} + 4\text{e}^-$ (Ionization - the Anode reaction)

At the *anode* - a location on the interface between the metal and the water (or between the metal and wet wood) two iron ions - iron atoms each minus two of their electrons - go into solution in water, leaving behind the four free electrons (which can travel freely through the solid metal but which cannot travel in water). This is the place on the metal surface where the solid metal is physically consumed.

Step 2: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \Rightarrow 4(\text{OH})^-$ (Oxygen reduction - the Cathode reaction)

At a nearby location on the metal-water interface, the *cathode*, one oxygen molecule and two water molecules combine with the four excess free electrons from the Step 1 to form four hydroxyl ions in the water.

Step 3: $2\text{Fe}^{++} + 4(\text{OH})^- \Rightarrow 2\text{Fe}(\text{OH})_2$ (Hydroxide formation)

Two iron ions in solution combine with four hydroxyl ions in solution to form iron hydroxide - wet rust. The rust typically deposits on the metal at the metal-water interface.

Step 4: $2\text{Fe}(\text{OH})_2 \Rightarrow 2\text{FeO} + 2\text{H}_2\text{O}$ (Drying of Hydroxide to Oxide)

Eventually, the iron hydroxide may dry out to form iron oxide - dry rust.

The series of reactions above is called **electrochemical corrosion**. Note that this sequence of four reactions gives exactly the same end result as direct oxidation - that is, iron and oxygen combine to form iron oxide. The water that entered in Step 2 was recovered in Step 4; it acted only as a catalyst - a facilitator - allowing the oxidation of the metal to occur at room temperature.

The reactions of electrochemical corrosion involve **electrons** and **ions**. **Electrons** are subatomic particles with a single negative charge - they can move freely through metals and they are the carriers of electric current in metals. **Ions** are atoms or groups of atoms that have gained or lost one or more electrons, giving them a net electric charge. Ions are many thousands of times larger than electrons; they are the carriers of electric current through water or through porous wet materials like wet wood (and the human body). The water (or wet wood) that connects the anode and cathode surfaces and through which ions can move from one place to another is called the **electrolyte**.

In order for Step 1 - ionization, to continue, the free electrons that the ionization releases into the metal must be taken away, or else further ionizations would be stifled by the negative charge that would build up. Step 2 - the cathode reaction - consumes the extra electrons and allows Step 1 to continue. Note that Step 2 requires oxygen. Without oxygen dissolved in the electrolyte, most types of wet corrosion cannot continue.

Electrochemical corrosion also requires that ions move through the electrolyte between the sites of the anode and cathode reactions. Because of their much greater size, ions do not move nearly as easily through electrolytes as electrons move through metals. If only the ions that are involved in the anode and cathode reactions were available for this ion current flow, the corrosion rate would be quite slow. The high concentration of positive sodium and negative chloride ions in seawater makes salt water much more corrosive than fresh water, primarily by providing many more charge-carriers.

Since these reactions involve the movement of electrically-charged particles they also constitute an electric circuit - in this case referred to as an **electrochemical cell**. This circuit has two legs - one leg is in the metal, with free electrons moving from the anode reaction site to the cathode reaction site; the other leg is in the water or wet wood (the electrolyte), with positive ions moving from the anode interface toward the cathode interface, and negative ions moving in the other direction. Every case of electrochemical corrosion is also a closed electrical circuit. Electrons move only through metals and ions move only through electrolytes. Both types of electric current flow are required for an electrochemical circuit or cell to operate.

When a particular metal or alloy corrodes by the process described above - electrochemical corrosion resulting from oxygen reduction without any outside influences (to be discussed below) - we call this process **Simple Electrochemical Corrosion**, or just **Simple Corrosion**. **Figure 1** illustrates the process.

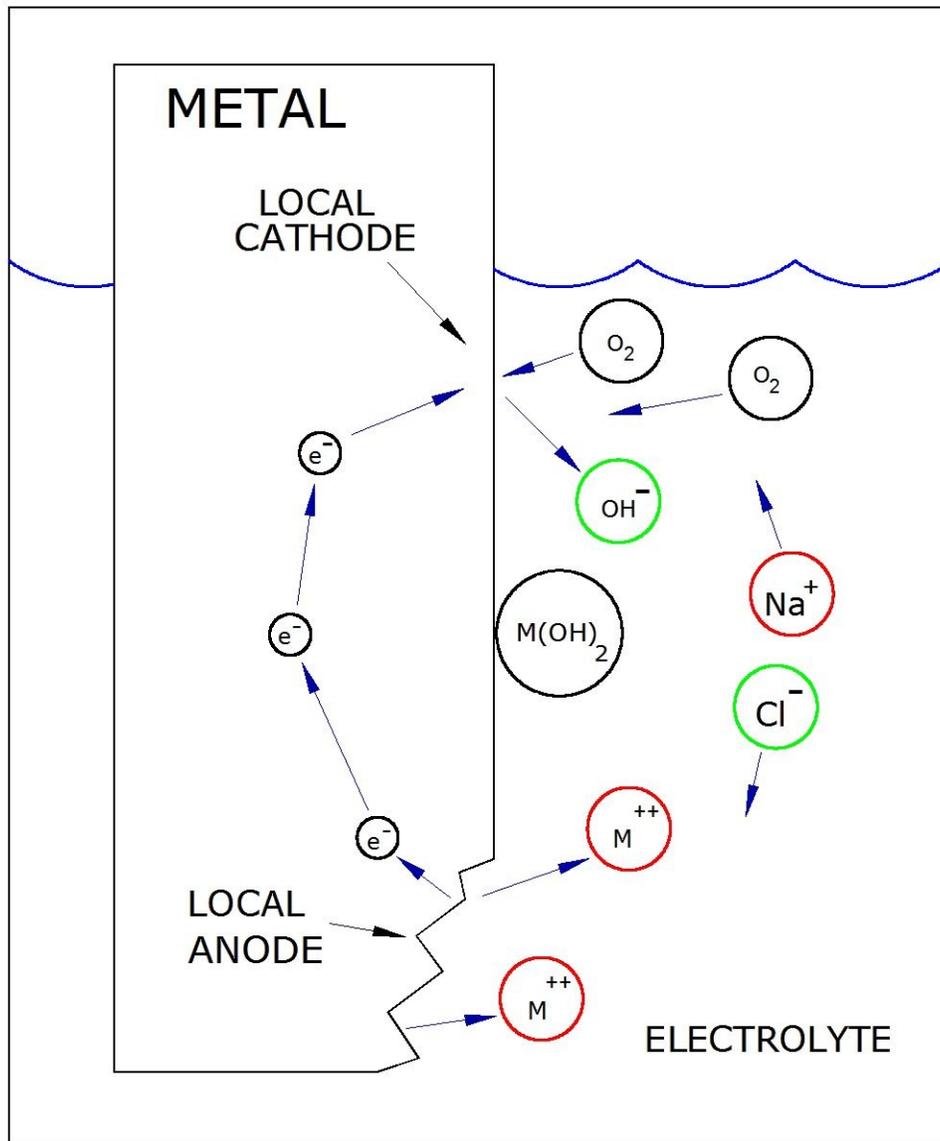


Figure 1 Simple Electrochemical Corrosion

e^- are electrons

M^{++} are ions of the corroding metal in solution in the electrolyte

O_2 are oxygen molecules dissolved in the electrolyte

$(OH)^-$ are hydroxyl ions produced by the cathode reaction

Na^+ and Cl^- are sodium and chloride ions, respectively, present in sea water

At the local anodes, the solid metal is going into solution as metal ions, the solid metal is being consumed, and excess free electrons build up. In the metal, the excess free electrons from the anode reaction travel to the local cathodes where they are consumed by the cathode reaction. The electron current in the metal

(negative upward) is balanced by ion current in the electrolyte (negative downward and positive upward), forming an electric circuit. Hydroxyl ions from the cathode reaction and metal ions from the anode reaction often meet and combine to form metal hydroxides (corrosion product films) on the surface of the metal.

The Galvanic Series

When a metal is first exposed to corrosive conditions (water or wet wood), the Anode reaction (Reaction #1 above - Ionization) and the Cathode reaction (Reaction #2 above - Oxygen Reduction) are slightly out of balance for a short time. This results in a slight accumulation or depletion of free electrons in the metal that causes a measurable shift in the metal's electrical potential or voltage. Once the corrosion begins, the Anode and Cathode reactions then proceed at equal rates, preventing any further accumulations or depletions of charged particles, but that initial potential shift persists. This potential varies from one individual metal or alloy to another, so that each metal or alloy undergoing electrochemical corrosion in a particular electrolyte like sea water has a unique, characteristic, and fairly predictable electrical potential that can be measured easily with simple equipment. This potential is traditionally called the metal's **Corrosion Potential** or **Freely Corroding Potential**. Both of these terms are confusing, because a metal exhibiting this potential is not necessarily corroding at any significant rate. The term **Galvanic Potential** is also sometimes used. **Natural Potential** is a better term. The list of metals with their natural potentials in oxygenated sea water is called the **Galvanic Series**. (see **Table 1**).

Table 1 - THE GALVANIC SERIES IN SEAWATER

METAL	CORROSION POTENTIAL RANGE (mV to Ag/AgCl)	
Graphite	+300	+200
Platinum	+250	+190
Stainless Steel UNS20910 ("Nitronic 50", "Aquamet 22")	+60	-250
Hastelloy C	+80	-30
Titanium	+60	-50
Ag/AgCl Reference Cell	(defined as)	0
Stainless Steel Type 316 (passive state)	0	-100
Stainless Steel ASTM 630 (17-4PH) "Aquamet 17"	+130	-30
Stainless Steel ASTM 564 (19-4PH)	+130	-30
Nickel 400, Nickel 500 (NiCu) ("Monel")	-40	-140
Stainless Steel Type 304 (passive state)	-40	-140
Nickel 200	-100	-200
Nickel 625 (NiCr) ("Inconel")	-140	-170
Copper-Nickel (CuNi) (30% Ni) C715	-180	-230
Lead	-190	-250
Copper-Nickel (CuNi) (20% Ni) C710	-190	-250
Copper-Nickel (CuNi) (10% Ni) C706	-210	-280
Stainless Steel Type 410 (passive state)	-260	-350
Cast "M" Bronze C922	-240	-310
Cast ASTM B62 Bronze (Leaded Red Brass) C836	-240	-310
Cast "G" Bronze C903	-240	-310
Silicon Bronze C655	-260	-290
Cast "Manganese Bronze" C865	-270	-340
Aluminum Brass	-280	-360
Admiralty Brass	-280	-360
50-50 Lead-Tin Solder	-280	-370
Copper	-300	-370
Tin	-310	-330
Muntz Metal	-300	-400
Wrought Red Brass C230	-300	-400
Wrought Yellow Brass	-300	-400
Wrought Naval Brass C464 ("Tobin Bronze")	-300	-400
Cast Nickel-Aluminum Bronze C958	-310	-420
Aluminum Bronze	-310	-420
Nickel 625 (NiCr) ("Inconel") (active state)	-350	-460
Stainless Steel Type 316 (active state)	-430	-540
Ni-Resist	-460	-580
Stainless Steel Type 304 (active state)	-460	-580
Cast Iron	-600	-710

Wrought Iron	-600	-710
Carbon Steel (Mild Steel)	-600	-710
Cadmium	-700	-730
Aluminum Alloys	-760	-1000
Zinc	-980	-1030
Mil-Spec Zinc Anodes	-1030	-1050
Aluminum Anodes (Al + 5%Zn)	-1100	
Magnesium & Alloys	-1600	-1630

(This table is based on the Galvanic Series presented in ABYC Standard E-2)

As a very general rule, metals with more negative natural potentials are more susceptible to corrosion, and those with more positive natural potentials are more resistant to corrosion, but there are many exceptions to this rule. Therefore, the Galvanic Series should not be used to predict the relative sea-water corrosion rates of the various metals and alloys. For example, note that steel would be theoretically more stable than zinc, based solely on steel's more positive natural potential. However, in real life the corrosion rate of steel in seawater is much greater than that of zinc, so much so that zinc is actually used as a corrosion-resisting coating on steel in certain marine environments.

The Natural Potential of a metal is measured by means of a voltmeter and a reference cell (in seawater, the reference is usually a silver-silver chloride (Ag/AgCl) cell). The standard Galvanic series lists natural potentials relative to the Ag/AgCl cell, but other references (like zinc) can be and are sometimes used. The potentials in the Galvanic Series can be shifted by a constant amount to accommodate other reference cells. **Figure 2** shows how the potentials listed in the Galvanic Series are measured.

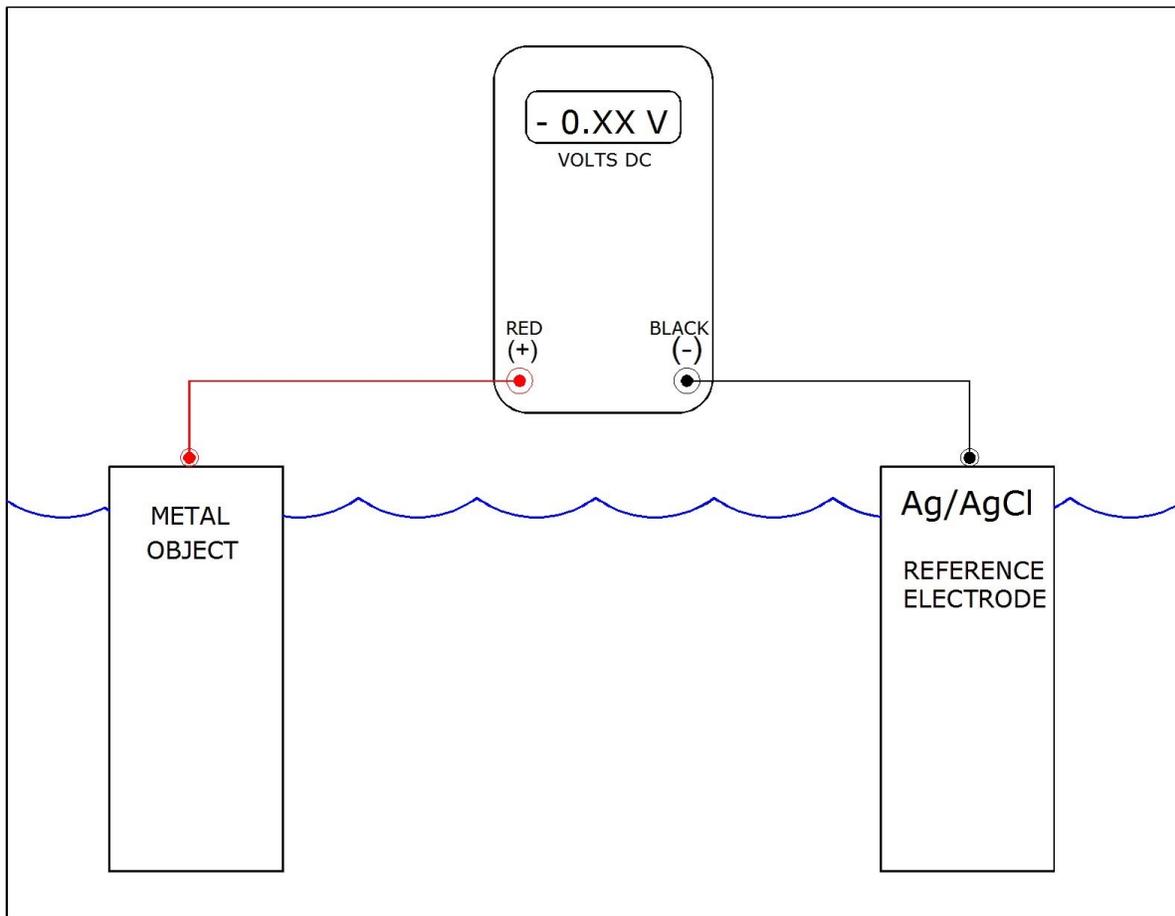


Figure 2 - Measuring a metal object's potential to a reference cell.

The wire lead of the Reference Cell is connected to the Common or black or (-) terminal of a digital multimeter and the cell is immersed in the electrolyte close to the metal to be measured. A probe is connected to the Volts-Ohms, or red, or (+) terminal of the meter and is touched to the metal. The meter is set to read DC volts or DC millivolts. The reading from an isolated object of a known metal immersed in seawater should correspond fairly closely to the Natural Potential of that metal listed in the Galvanic Series.

Galvanic Corrosion and Sacrificial-Anode Cathodic Protection

Now let's consider two different metal objects, each undergoing simple electrochemical corrosion in the same body of electrolyte. These objects are of different metals or alloys and each object is corroding at its own characteristic rate and each has its own characteristic natural potential resulting from the natural buildup or depletion of free electrons. For the sake of example, we will assume that the metal with the more negative natural potential is zinc and the metal with the more positive natural potential is copper. The copper object and the zinc object,

even if in close proximity in the electrolyte (which might be water or wet wood), have no influence on each others' corrosion rates.

If we now connect the two metal objects together with a metal wire or bring them into direct metallic contact, negatively charged electrons will flow along the wire or connection from the initially-more-negative zinc to the initially-less-negative copper. This current will increase until the electrical potentials (voltages) of the two objects nearly equalize at a common potential somewhere between their former individual natural potentials (exactly where depends on the relative areas of each metal exposed to the electrolyte and on some other factors, and is a function of the particular situation). This flow of electrons will continue as long as the objects stay in electrical contact.

On each metal, the effect of the electron flow is to shift the previous equal balance of local anode and local cathode reaction rates. On the copper, the effect of the extra electrons arriving is to increase the cathode reaction rate and to decrease the anode reaction rate. Because the corrosion rate *is* the anode reaction rate, the corrosion of the copper decreases and possibly stops altogether. On the zinc, the effect of the electrons departing is to decrease the cathode reaction rate and to increase the anode reaction rate. Again, since the anode reaction rate is the corrosion rate, this increases the rate of corrosion of the zinc. The zinc is now undergoing what we call **Galvanic Corrosion** (in addition to the Simple Corrosion that was already occurring, and which continues). And the copper is receiving what we call **Sacrificial-Anode Cathodic Protection**. The entire system is called a **Galvanic Cell**. We refer to the copper as the *cathode* of the galvanic cell and to the zinc as the *anode* of the cell. **Figure 3** shows an example of a galvanic cell comprising copper and zinc.

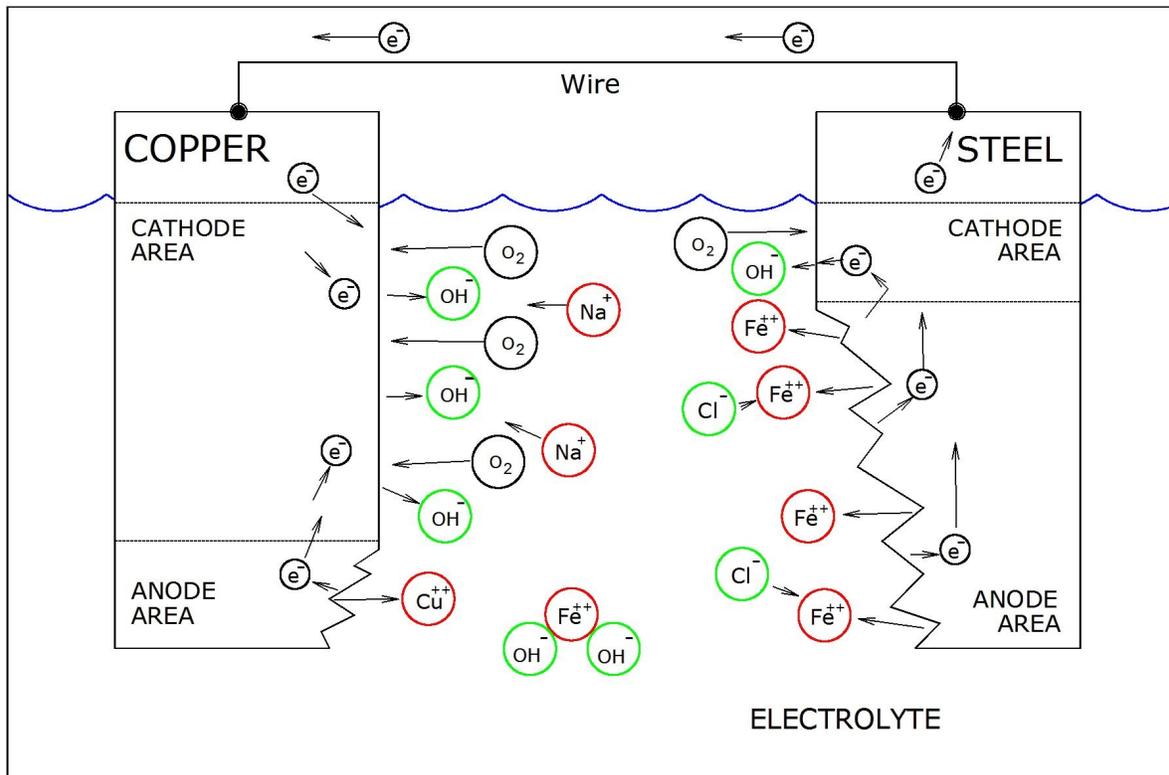


Figure 3 - The Galvanic Cell - Galvanic Corrosion and Sacrificial-Anode Cathodic Protection

A steel object and a copper object are immersed in the same body of electrolyte and connected by an electron-conducting metallic link. Since the steel initially (before the wire was connected) had a more negative potential than the copper, electrons flow from the steel to the copper at a rate that will almost equalize the potentials of the two metals. The electrons arriving at the copper shut down anodes and convert them to cathodes, decreasing the corrosion rate of the copper (possibly stopping the corrosion entirely). The electrons leaving the steel cause cathodes there to be converted into anodes, thus increasing the corrosion rate of the steel. The steel is undergoing Galvanic Corrosion - the copper is receiving Sacrificial-Anode Cathodic Protection.

In summary, for there to be a galvanic reaction between two metals:

1. They must have different natural potentials;
2. They must be immersed in the same body of electrolyte (in other words, they must be **electrolytically connected**) ; and
3. They must also be **electrically connected** by a wire or by some other direct metallic connection.

The rate of corrosion due to galvanic effects can be many times that of simple corrosion. The initial electrical potential difference (the “driving potential”) between the local anodes and local cathodes in a simple electrochemical cell is usually hundredths or at most a few tenths of volts. A glance at the Galvanic Series will show that the difference in the natural potentials of the anodes and cathodes of a galvanic cell may be one volt or more.

The intensity of galvanic corrosion depends on the relative exposed areas of the metals involved. For example, a large area of copper connected to a small area of steel will cause the corrosion rate of the steel to increase significantly, while a small area of copper connected to a large area of steel will usually have only a slight adverse effect on the steel. The ratio of cathode area (copper in this case) to anode area (steel in this case) is the **area ratio** of the cell. Looking at it from the point of view of the corroded metal, a large area ratio is referred to as an “unfavorable area ratio” because it causes more significant galvanic effects than a smaller area ratio.

Clearly, while galvanic corrosion is bad for the metal with the more negative natural potential, which is corroded, it is beneficial to the other metal. We use this principle to protect metals from corrosion by electrically connecting the metal we want to protect to another metal having a more negative natural potential, immersed nearby in the same body of electrolyte. The metal that is sacrificed protecting the other is typically zinc, but may also be aluminum, magnesium or even steel in some instances. The process is called Sacrificial-Anode Cathodic Protection. “Sacrificial” because the anode corrodes away (and is intended to corrode away) in the course of providing electrons to the protected metal. “Cathodic Protection” because the metal being protected becomes the cathode of a galvanic cell. The level of protection provided by sacrificial anode systems is generally regulated only by the surface area of the anodes; the duration of that protection is a function of the mass of the anodes.

The fundamental mechanism of cathodic protection is the electric current that passes through the interface between the metal and the electrolyte. This current is in the form of electrons arriving at the interface from the body of the metal, and being converted, via the cathode reaction, to ion current in the electrolyte adjacent to the surface. In the case of a cathodically-protected surface, electrons arrive at the interface from within the metal. Negative ions move away from the interface in the electrolyte and/or positive ions move toward the interface. If a certain current density (amps per unit area) is attained, then all of the local anode activity is shut down, the entire surface becomes a cathode, and corrosion is stifled.

Outside of a laboratory, it is not possible to measure the current density nor usually to even measure the total protective current. However, the cathode reaction occurring at the interface between the metal and the electrolyte acts like an electrical resistance. And as in any electric circuit, a current moving through a resistance produces a voltage drop. This voltage drop is measurable as a shift in the electrical potential of the metal object receiving the protection. And, fortunately, we can measure the potential of the protected metal quite easily with a *reference cell*.

It turns out that when the potential of a metal to be protected has been shifted, due to the application of cathodic protection, by about 200mV in the negative direction from the metal's Natural Potential (as listed in the Galvanic Series), then enough protective current has been established to provide more or less full protection from corrosion. The -200mV shift can be thought of as the voltage drop resulting from the protective current passing through the resistance of the cathode reaction.

For example, steel (with a natural potential of about -600mV to a Ag/AgCl reference cell) is considered fully protected when its potential has been shifted to at least -800mV by the application of cathodic protection. Aluminum, with a potential of about -750mV, is fully protected at a potential of at least -950mV. Various copper alloys, with natural potentials in the -250 to -300 mV range, are fully protected at about -450 to -500 mV.

In **Figure 3** (above) the copper is receiving Sacrificial-Anode Cathodic Protection.

Measuring the Potentials of Metal Objects Exposed to Electrolytes

It is important to understand that two metal objects immersed in a common body of electrolyte but not in electrical (metallic) contact do not constitute a galvanic cell. In Figure 4, each metal is undergoing Simple Electrochemical Corrosion without influence from the other, and each shows its natural potential to a reference cell.

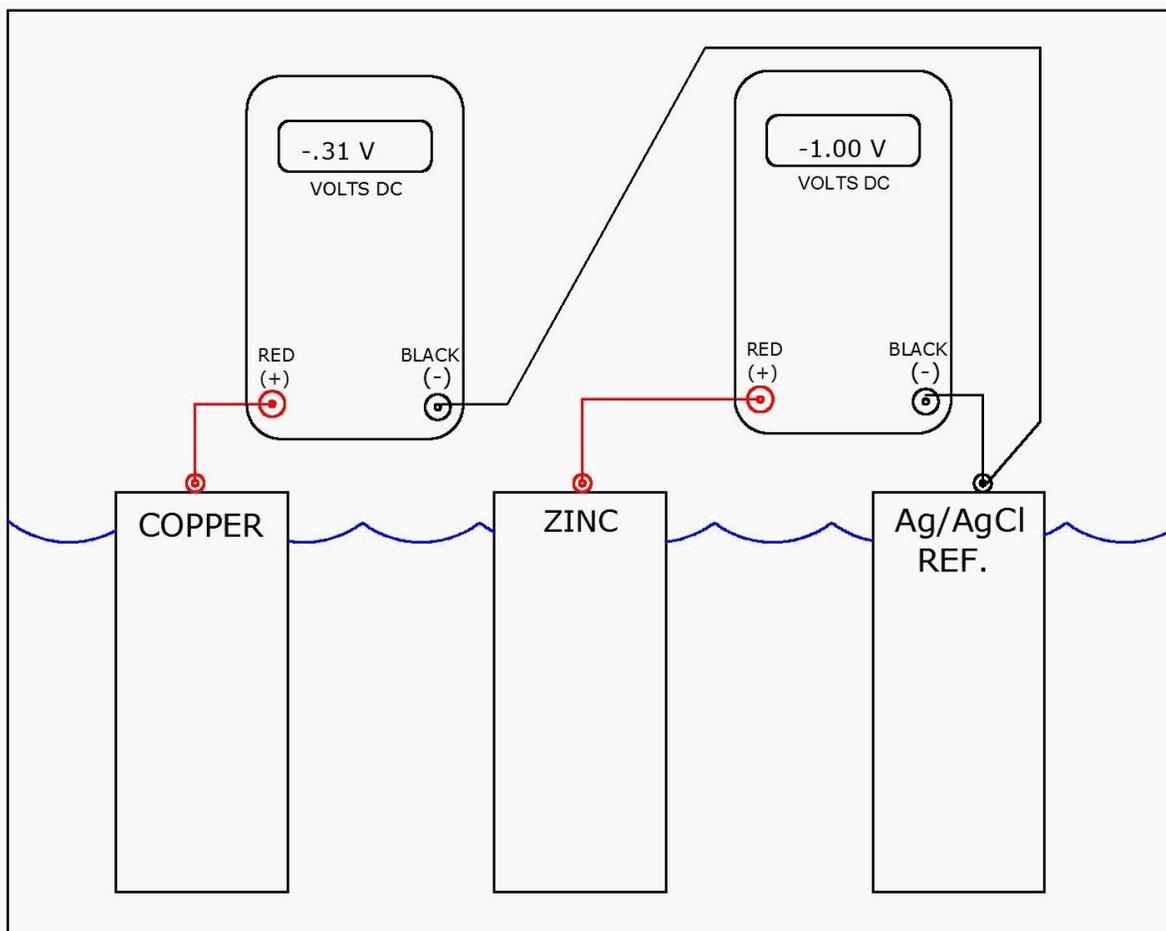


Figure 4 - Measuring the Potentials of Two Electrically-Isolated Metal Objects in a Common Body of Electrolyte using a Reference Cell

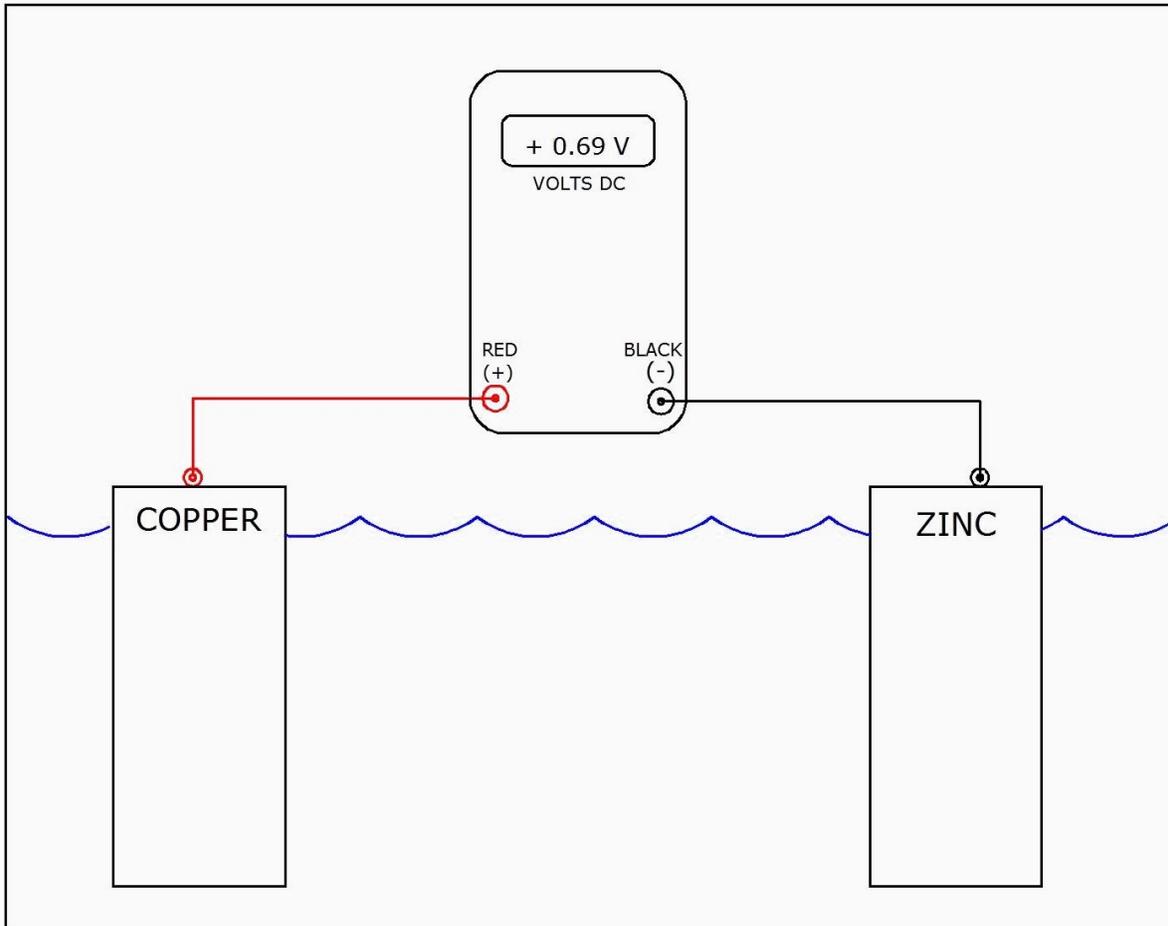


Figure 5 - Measuring the Potential Between Two Electrically-Isolated Objects in a Common Body of Electrolyte

Two objects of different metals are immersed in a common body of electrolyte but with no metallic electrical connection between them. They do not constitute a galvanic cell, they each show their natural potential to a reference cell, and they do not affect one another's corrosion rate

Figure 5 is simply another way of looking at the same situation shown in **Figure 4**, this time the meter measures the potential directly between the two objects, with no reference cell. Corrosion technicians often receive frantic calls from boat owners, surveyors, or marine electricians who have measured a DC electrical potential of maybe 500mV or so between two hull fittings or other objects (often between a propeller shaft coupling and the transmission coupling with the couplings separated), and who are alarmed, thinking that this indicates a terrible corrosion problem. As you can see, it is perfectly normal for there to be a potential between two objects that are not electrically connected, and this potential in fact indicates that at the time the measurement was taken, there was no galvanic interaction between them (because if

they were galvanically interacting, their potentials would be nearly equal). It also indicates that *when they are re-connected*, there will be a galvanic interaction somewhere.

In the case of the shaft couplings, the measured potential is usually simply the difference between the potentials of the shaft and propeller and the anodes on them and the potentials of the various immersed hull fittings that are electrically connected to the boat's negative ground point and thus to the engine block and the transmission.

When the two metals shown in **Figures 4** and **5** are connected into a cell by a metallic link, they now both show the same potential, which will be somewhere between their natural potentials. They now constitute a Galvanic Cell. See **Figure 6**.

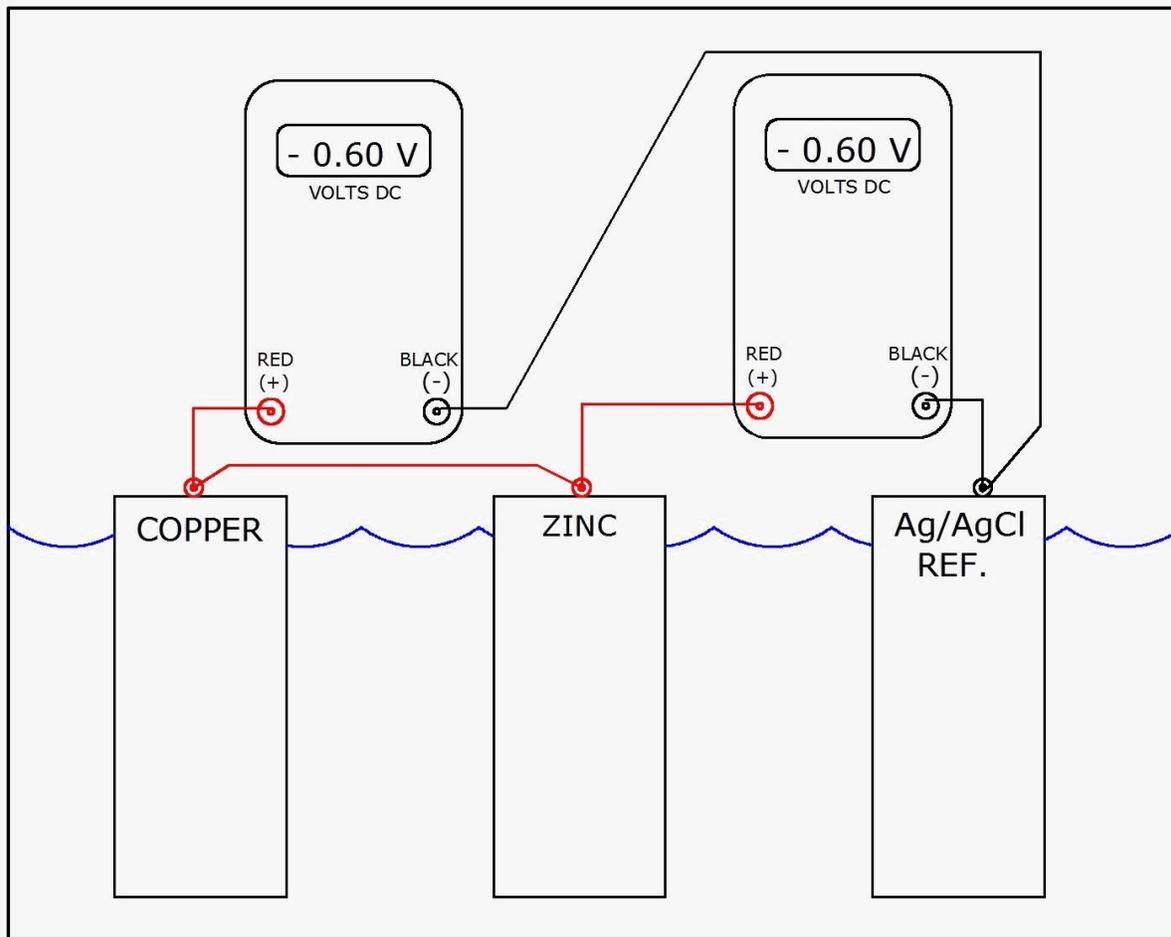


Figure 6 - Potentials of Electrically-Connected Metals (A Galvanic Cell) in a Common Body of Electrolyte

Two objects of different metals are immersed in a common body of electrolyte and are connected electrically by a wire. Therefore, they constitute a Galvanic Cell. They both show very nearly the same potential to a reference cell. The cell potential is between their Natural Potentials (the exact value is determined mainly by their respective exposed areas). Since the potential of the copper is 300mV more negative than its natural potential of -300 mV, it is completely protected from corrosion (a shift of at least 200mV in the negative direction from the natural potential indicates full cathodic protection). The potential of the zinc is more positive than its natural potential of about -1000 mV, which indicates that it is undergoing accelerated corrosion (Galvanic Corrosion in this case).

One note: In order to measure the galvanic potential shift accurately, the reference cell should be positioned as close as possible to the surface of concern, and as far as possible from other elements of the cell. This is because there is also a small voltage drop in the electrolyte due to the ion current passing between the anodes and the protected surface, and we don't want that

drop to be incorporated into the measurement of the potential shift, or it will give the impression that more protection exists than actually does. In the example above, if we're concerned with evaluating the level of protection of the copper, then the reference cell should be as close as possible to the copper and as far as possible from the zinc.

Stray-Current Corrosion and Impressed-Current Cathodic Protection

Let's now take again the case of two electrically isolated metal objects corroding independently by simple corrosion in the same body of electrolyte. Now we connect a DC current source between the two objects (on boats, DC current sources are usually at least 12 volts, sometimes more). The magnitude of the external voltage overwhelms any galvanic-level differences that may have existed between the two objects. Electrons are pumped into the object connected to the negative terminal of the current source, shutting down any local anodes, eliminating any corrosion, and establishing an intense cathode reaction over its entire surface. Electrons are extracted from the object connected to the positive terminal of the source, establishing an intense anode reaction over its entire surface, very likely resulting in a catastrophically-high corrosion rate.

The system we describe here is a **Supplied-Current Electrochemical Cell**. The object connected to the positive terminal of the source is undergoing **Supplied-Current Corrosion** which, if it is unintentional or inadvertent, as it often is, is usually called **Stray-Current Corrosion**. **Figure 7** shows a Supplied-Current Cell.

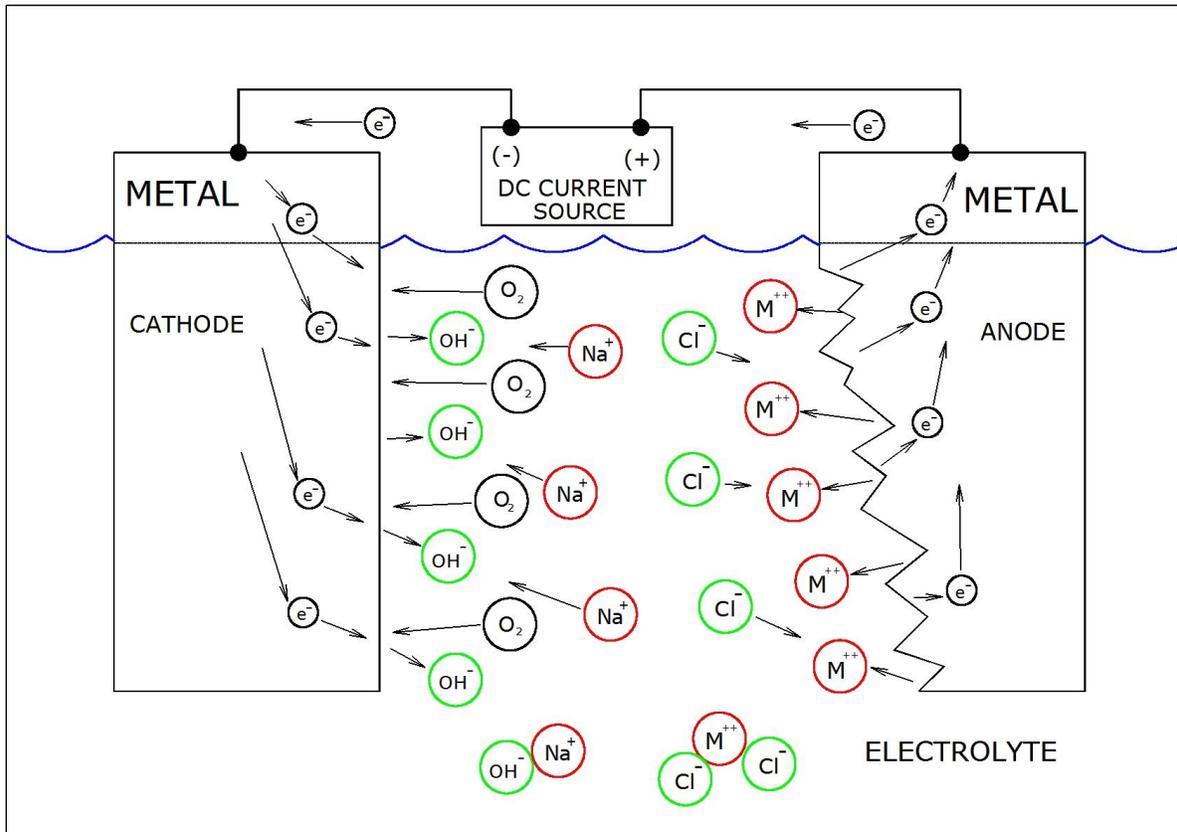


Figure 7 - The Supplied-Current Cell - Stray-Current Corrosion and Impressed-Current Cathodic Protection

Two metal objects, immersed in the same body of electrolyte, are connected to the positive and negative terminals, respectively, of a DC current source. The metal object (referred to as the *anode* of the cell) which is connected to the positive terminal suffers intense corrosion, usually called “Stray-Current Corrosion” because such connections are usually unintentional. The metal object (referred to as the *cathode* of the cell) which is connected to the negative terminal receives cathodic protection which, if it is intentional and if the current is controlled to maintain a proper level of protection, is called “Impressed-Current Cathodic Protection”.

In the case of a stray current cell operating in a boat environment, an intense uncontrolled cathode reaction occurs on the metals connected to the negative terminal of the current source - typically underwater metal fittings of the hull which are connected to the boat’s battery negative terminal via direct contact or via the bonding system. This intense cathode activity very often causes those fittings - the cathodes of the cell - to develop heavy calcareous deposits which may form a base for heavy marine growth.

Objects undergoing simple electrochemical corrosion usually experience significant corrosion in years or tens of years; those undergoing galvanic corrosion are often significantly corroded in months, and those undergoing stray-current corrosion may be corroded badly in hours or days. Instances of severe stray-current corrosion are virtually always related to Direct Current (DC) electrical faults on board boats. Thankfully, they are rare. Many (even most) corrosion problems on boats that are initially attributed to stray-current corrosion turn out, on further investigation, to actually be galvanic corrosion or even simple electrochemical corrosion.

Just as there was a bright side to the galvanic cell - the possibility of protecting metals from corrosion with sacrificial anodes - so also the supplied-current cell provides us with a method to prevent corrosion. The metal connected to the negative side of a DC current source (the positive side of which is connected to another metal object in the same body of electrolyte) is protected from corrosion. If that object connected to the positive side of the source was simply a piece of copper or steel or aluminum or zinc, it would be corroded away in a very short time and the protection scheme wouldn't work very well. However, certain metals like titanium and platinum can stand up to being an anode of a supplied-current DC cell without corroding away themselves - one or more alternate anode reactions involving water molecules and ions in the water occur instead.

This process is called **Impressed-Current Cathodic Protection**. The protective current flow in such systems is virtually always electronically regulated to provide the correct level of protection (that is, a 200mV negative shift in potential). These systems are powered from the vessel's electrical system, so the protection lasts indefinitely (as long as the batteries stay charged). The control system uses a reference cell permanently installed through the hull.

The metal object connected to the negative side of the current source in **Figure 7** (above) is receiving Impressed-Current Cathodic Protection

The shift in the potentials of metals when they become part of galvanic or supplied-current cells can provide simple and easily obtained diagnostic data. If a metal object shows a potential more negative than its natural potential as shown in the galvanic series, then it is the cathode of a cell, it is receiving cathodic protection from somewhere, and its corrosion rate is less than it would be if it was immersed by itself in the electrolyte. If a metal object shows a more positive potential than its natural potential, then it is the anode in a galvanic or supplied-current cell and its corrosion rate is greater than it would be in isolation, and there's usually something wrong.

Replacement Corrosion

The oxygen reduction reaction shown above as step (2) in the electrochemical corrosion process is certainly the most common cathode reaction in marine electrochemical corrosion, but it is not the only one possible. If a metal is immersed in an electrolyte that contains ions of a more stable metal, for example, a piece of steel in an electrolyte containing copper ions, the more stable copper ions will accept electrons from the solid steel, plating out as solid copper (that's the

cathode reaction), and a corresponding number of ions of the formerly solid steel will go into solution as iron ions (that's the anode reaction). In effect, the steel is replaced atom by atom by the copper, and that's why the process is sometimes called **Replacement Corrosion**. But the replacement is usually only the beginning of a much more serious corrosion process. The deposited copper on the steel sets up small galvanic cells that accelerate the corrosion rate of the steel even after the copper ions are depleted from the electrolyte, or the electrolyte is changed and the actual replacement reaction has ended. The pitting of the steel due to this galvanic corrosion usually accounts for more corrosion of the base metal than did the actual replacement. Replacement corrosion is also sometime called "Deposition Corrosion". **Figure 8** shows the mechanism of Replacement Corrosion.

In wood boats, replacement corrosion can be responsible for accelerated corrosion of galvanized-steel fasteners embedded in wood containing copper-based wood preservatives. In metal boats, slight amounts of copper dissolved in fresh water can deposit on steel or aluminum surfaces in fresh-water tanks and can eventually cause galvanic pitting of the tanks. Condensation dripping from copper pipes or copper-alloy sea water plumbing fixtures like sea strainers onto steel or aluminum hull plating can cause galvanic pitting from the inside. Coins, copper-alloy fasteners, or cut-off ends of stranded copper electrical wire dropped in the bilge can also cause galvanic pitting of steel or aluminum hulls from the inside.

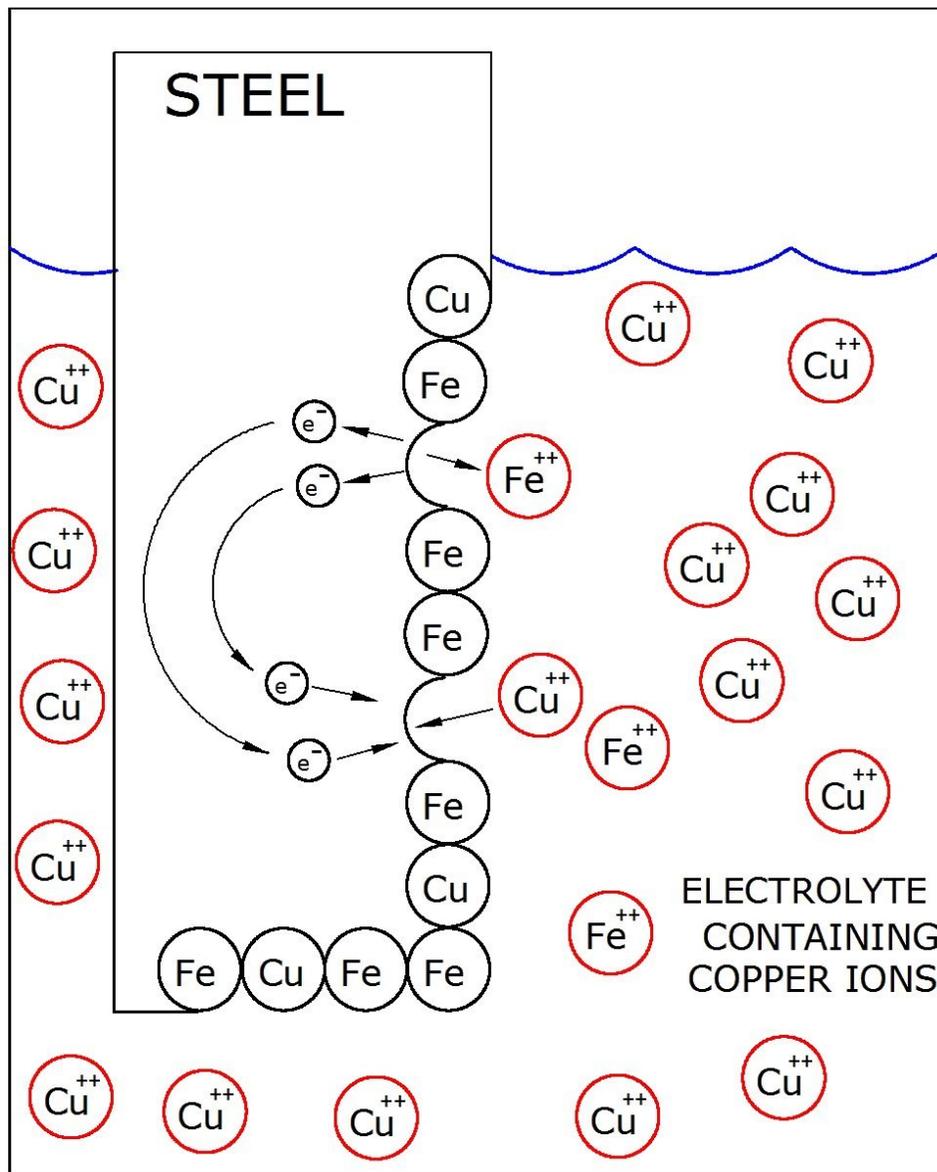


Figure 8 - Replacement (Deposition) Corrosion

A metal object (steel in this example) is immersed in an electrolyte containing ions of a metal with a more positive natural potential (copper in this example). A local electrochemical cell is formed, with the ionization of iron being the anode and the plating of solid copper from the electrolyte onto the metal surface being the cathode. The steel is, in effect, “replaced” atom-by-atom by the copper. While the replacement process can continue only as long as there is still copper in the electrolyte, even a small amount of copper deposited on the surface of the steel then serves as the cathodes in a normal galvanic cell, accelerating the corrosion rate of the steel even after the replacement reaction has ceased.

AC Stray-Current Corrosion

It's possible to construct a supplied-current electrochemical cell in which alternating-current (AC) is imposed across two or more objects in a common body of electrolyte by an outside AC source, and which causes the metals to corrode. However, corrosion by AC is much less serious than by DC, and really only affects a few metals and then only at quite high current densities that are hard to achieve in an actual stray-current situation in the field. Most corrosion originally ascribed to AC stray currents turns on further investigation to be garden-variety galvanic corrosion or occasionally DC stray-current corrosion.

Electrolysis

It is not uncommon to hear virtually every corrosion-related process referred to as "electrolysis". Electrolysis is, properly, the breakdown of water into its constituents, hydrogen and oxygen, at the electrodes of a supplied-current electrochemical cell. *Electrolysis is something that happens to the water.* The things that happen to the *metal*, with which we are most concerned, are more accurately described by proper, specific, and unambiguous terms - simple corrosion, galvanic corrosion, stray-current corrosion, cathodic protection, crevice-corrosion (see below), etc.

Part 2 - Corrosion Prevention Practice in Wood Hulls

The Effects of Cathodic Protection on Wood Hulls

When a metal fitting of a hull is cathodically protected, the oxygen reduction reaction (Step 2 of the electrochemical reactions presented above) is established over its wetted surface. That reaction produces hydroxyl (OH^-) ions. If the metal fitting is in contact with wet wood and if there is little flushing to carry away the hydroxyl ions, the accumulating ions cause strong alkaline (basic or high-pH) conditions that dissolve away the lignin - the binding resin of the wood, leaving behind loose white-colored bundles of less-severely-damaged cellulose fibers. The process by which the wood deteriorates is called **delignification**. It very often creates serious structural problems on boats with uncontrolled sacrificial-anode cathodic protection systems. The problem is sometimes referred to as “electrolysis rot”. Because “delignification” is such a tongue-twister, “Cathodic Wood Damage” is probably the best term to describe the phenomenon.

The wood affected is typically inside the hull, below the waterline but above the bilge-water, where there is plenty of moisture but little or no flushing or dilution. It occurs in close proximity to cathodically-protected fittings that pass through the hull and contact wet wood inside the hull, like thru-hull fittings, prop-shaft and rudder-shaft stuffing-boxes, strut bolts, etc. and it is caused by the effects of the cathodic current flow to those fittings. In many cases the cathodic protection is inadvertent - the fittings happen to be connected to the boat’s cathodic bonding system for protection from stray-current corrosion, and there are sacrificial anodes also connected to the same bonding system (see below for details). Also, in most cases the metal hull fittings around which the problem occurs cannot actually benefit from the cathodic protection applied to them, because they are not sufficiently exposed to the electrolyte that much ion current can reach their surfaces. However, the small amount of current that does reach them through wet wood is enough, over months or years, to cause the chemical changes that damage the wood.

The worst cases of cathodic wood damage are those that are mis-diagnosed as being due to inadequate cathodic protection. Such an incorrect diagnosis often leads to further increases in the level of protection through the addition of even more sacrificial anodes, which of course only aggravates and accelerates the problem. (This is, unfortunately, not a unusual occurrence.)

Many vessels with DC electrical systems have what is called a **bonding system** (called the **Cathodic Bonding System** in the ABYC Electrical Standards). A bonding system is a network of fairly heavy wires that connects metal hull fittings directly to the boat’s common DC negative ground point. The purpose of the bonding system is to prevent DC stray current corrosion of underwater metal fittings. If for some reason there is an inadvertent connection inside the boat between a DC positive conductor and a fitting that allows a DC fault current (a “stray current”), the bonding system will provide a direct metallic path for that fault current, hopefully tripping an overcurrent protective device (a fuse or circuit breaker) and cutting off the fault. Without the bonding connection, the fitting would become the anode of a supplied-current

cell (the propeller and shaft would typically become the cathode, since they are connected via the engine block to the battery negative terminal), and the fitting receiving the stray current would be corroded catastrophically in a short time. The current flowing in such a cell, while sufficient to cause severe corrosion, is usually not large enough to trip a circuit breaker, so it continues until the battery is depleted or possibly until the boat sinks because the fitting is consumed. **Figure 9** shows how stray-current corrosion occurs on a boat. **Figure 10** shows how the Cathodic Bonding System prevents stray-current corrosion

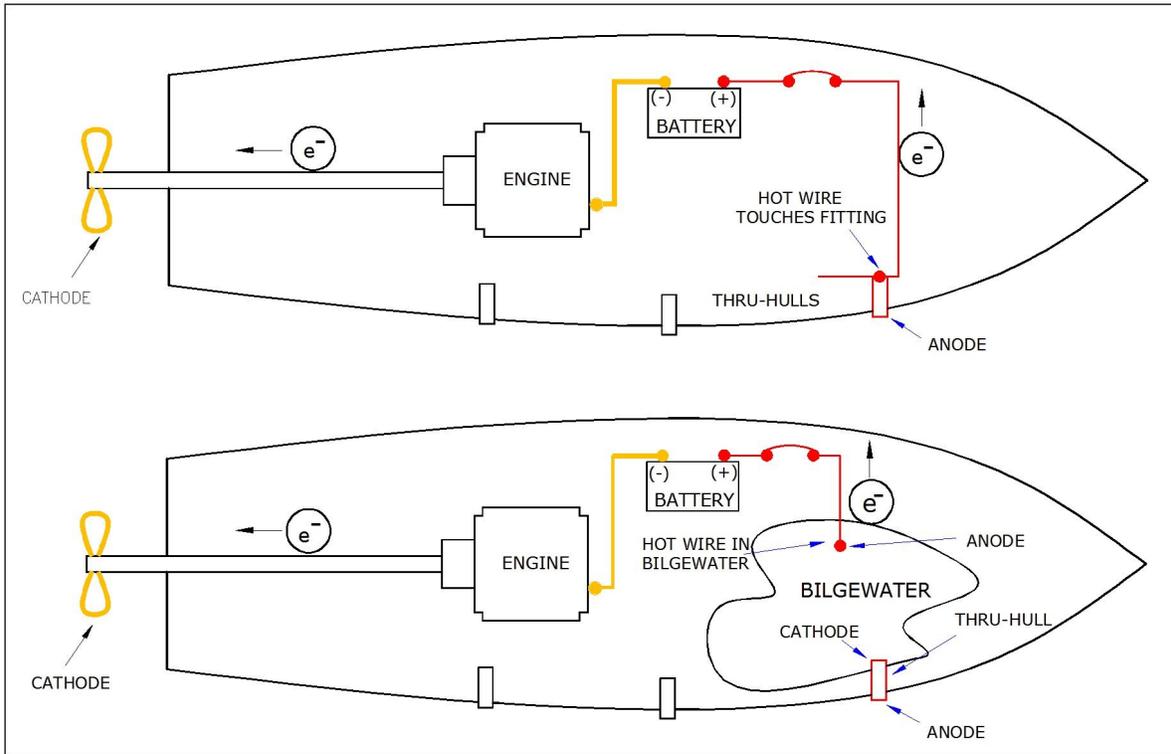


Figure 9 - Stray-Current Corrosion of Metal Hull Fittings

In the upper view, a DC-positive wire makes direct contact with an underwater hull fitting. The fitting becomes the anode of a supplied-current cell, and corrodes rapidly. The current is typically enough to cause catastrophic corrosion, but it is usually not high enough to trip a breaker or blow a fuse.

In the lower view, an energized DC device (like a submersible bilge pump) in the bilge water develops a DC fault to a metal part (usually the vertical pump shaft) which is exposed to the bilge water. The stray current travels as ion current through the bilge water to a hull fitting that is exposed to both the bilge water and the outside water, resulting in stray-current corrosion of the fitting where it is in contact with the outside water.

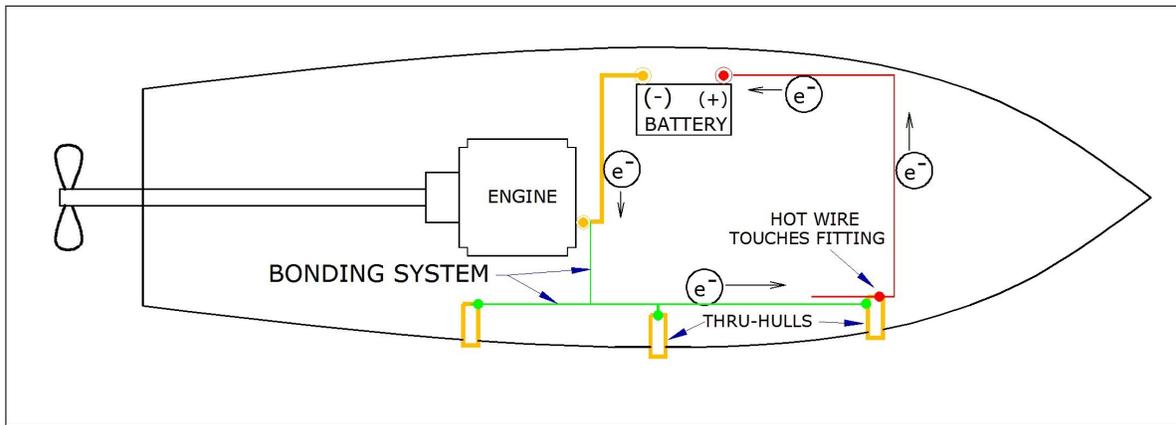


Figure 10 - The Cathodic Bonding System - Decreasing the Risk of Stray-Current Corrosion

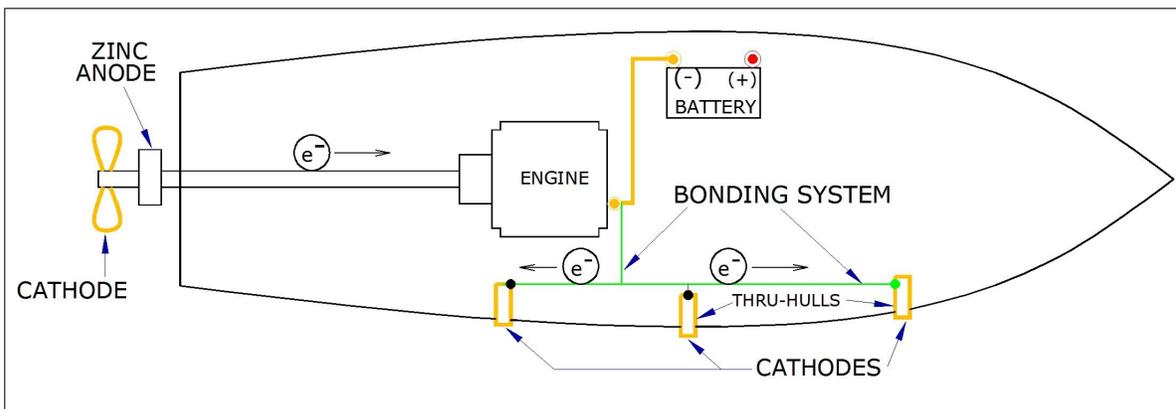


Figure 11 - Cathodic Protection Distributed by the Cathodic Bonding System

Figure 10 shows how the Cathodic Bonding System prevents stray current corrosion of a hull fitting receiving a stray current. When the stray current reaches the fitting, the current is conducted directly back to the boat's negative ground point by the bonding wire. This prevents most of the stray current that would otherwise travel through the water. And, hopefully, the direct bonding connection conducts enough stray current to trip a circuit breaker or blow a fuse, thus cutting off the fault current entirely.

Figure 11 shows how the bonding system distributes cathodic protection from an anode on one underwater fitting to other underwater fittings in other parts of the hull. This is sometimes intentional, sometimes inadvertent. Cathodic wood damage on wood hulls often occurs at hull fittings that unintentionally receive cathodic protection via the bonding system.

In wood hulls the bonding system, unfortunately, can also cause problems. Somewhere on the bonding system network there are usually one or more sacrificial anodes, protecting various susceptible underwater metal fittings, such as propeller shafts, propellers, struts, etc. The protective current from these anodes goes not only to the fitting they are intended to protect, but also to all underwater metal fittings that are connected, via the bonding system, to the fitting with the sacrificial anode. If some of those fittings are in contact with wood, and particularly if they penetrate the hull above the bilge water but below the waterline, then the wood around those fittings is susceptible to cathodic wood damage. The situation is usually worst on hulls with sacrificial-anode cathodic protection, which is usually not controlled, and which often results in a lot more protective current than is actually necessary to keep the metal parts from corroding. More protective current means more hydroxyl ion generation at the cathodes, and more damage to the wood. Most wood hulls inspected by the Coast Guard are fairly small, and small wood hulls rarely have impressed-current cathodic protection systems, which control the level of protection and which therefore minimize (but do not entirely eliminate) cathodic wood damage. (**Figure 11** shows how cathodic protection is distributed to hull fittings by the bonding system).

With a wood hull it is often impossible to do everything, that is, to maintain an effective bonding system to protect against stray currents, to maintain cathodic protection for fittings that require it, and to prevent wood damage around cathodically-protected fittings. Typically, a compromise must be reached.

The first step is to eliminate from the bonding system any fittings that would be likely to cause cathodic wood damage to surrounding wood if they were cathodically protected, but that do not require or that cannot benefit from cathodic protection and that are not in danger of receiving any stray current. Fittings well above the bilge-water level and not in proximity to any wire runs are usually pretty safe from stray currents (aside from direct contact with chafed wires, stray currents originating at submersible bilge pumps are the most likely source of stray currents). Thru-hulls, seacocks, and other cast marine plumbing fittings are inherently very corrosion-resistant and can get along quite well without any cathodic protection.

The next step is to separate the bonding system from the underwater metals that do require cathodic protection, and to provide the anodes only to those parts. On most wood hulls, the propeller shafts and propellers do benefit from cathodic protection. The shafts can be electrically isolated from the transmissions by simple and fairly inexpensive electrically-insulating couplings (one well-known brand is the DriveSaver®). This allows cathodic protection of the shafts and props via shaft anodes, without applying that protection to other fittings that are connected to the bonding system. One occasional problem with this approach is that there is sometimes inadvertent metallic contact between the shaft and the inside of the stuffing box fitting, which then applies protection to the stuffing box and can lead to cathodic wood damage inside the hull where the stuffing box bolts to the hull. A simple electrical continuity measurement will show this inadvertent contact, which can often be eliminated by a slight alignment adjustment if it is known. The same problem can occur when cathodically-protected metal rudder shafts (and metal shafts of cathodically-protected metal rudders) contact their stuffing boxes, which often have very little radial clearance.

Shaft struts present a difficult decision. They are usually cathodically protected and bonded via a bonding wire which is connected to the strut mounting bolts inside the hull and to outside hull anodes connected elsewhere on the bonding system. Without cathodic protection, struts, which are often made of manganese bronze for strength, may be subject to corrosion; with cathodic protection the backing blocks and nearby planking often suffer. Bronze struts will usually have a long life without protection, but some alloys are susceptible to dezincification without cathodic protection. Occasionally, elaborate schemes are devised involving gaskets between the struts and the hull, plastic sleeves around mounting bolts, and plastic washers under the nuts of the mounting bolts to prevent any contact of the strut body or its fasteners with the wood parts of the hull.

Anodes for Cathodic Protection

Sacrificial-anode cathodic protection is usually accomplished with zinc anodes. The alloy from which the anodes are made is critical. Very small amounts of certain impurities can seriously impair the performance of anodes and very small and carefully-controlled amounts of certain other alloying elements are necessary for good performance. All zinc anodes should meet the MIL-SPEC for anodes. Zinc anodes have a natural potential of about -1030 mV relative to an Ag/AgCl reference cell.

There are two other alloys sometimes used for cathodic protection. Magnesium anodes (not pure magnesium, but a special alloy) are used for cathodic protection of steel and aluminum hulls in fresh water, and sometimes for hulls that operate in sea water, but which moor or dock only primarily in fresh water. Magnesium anodes have a natural potential of about -1600 mV. Magnesium anodes should never be used on wood boats except in rare intentionally-and-carefully-designed applications, as they can provide high levels of protection and can supply large amounts of protective current that in many situations would cause severe cathodic wood damage to wood in contact with protected fittings.

Aluminum anodes (not pure aluminum, but a special alloy of aluminum, zinc, and indium) are used to protect steel and aluminum in both fresh and sea water. They have a natural potential of about -1100 mV to Ag/AgCl. They are useful in vessels that pass regularly from sea water to fresh water, and which may moor in either. Zinc anodes often form an adherent surface film in fresh water and they do not always spontaneously re-activate on return to sea water. Aluminum anodes work in any water. However, because of they have a more negative potential than zinc anodes, they are also more likely than zinc to cause cathodic wood damage if used on a wood boat. The only parts of most wood boats that really need cathodic protection in fresh water are stainless-steel shafts. Aluminum anodes could be used in these applications as long as the shafts are isolated from metallic electrical contact with any metal hull fittings that are in contact with wood.

Controlled Sacrificial-Anode Systems

At least one manufacturer makes a sacrificial-anode cathodic protection system that incorporates a permanent reference cell and an automatic control system, like that in an impressed-current system, to provide the correct level of protective current from a large hull-mounted anode or anodes to the underwater metals. The controller is generally placed between the anode or anodes and the bonding system, and it controls the flow of current from the anode(s) to metal fittings connected to the bonding system. Such a system has the advantage over simple sacrificial-anode systems in that it does not overprotect, which minimizes cathodic wood damage. It can use a large amount of zinc, to ensure long anode life, without the danger of overprotection. Unlike impressed-current systems it requires no electric power from the boat's electrical system, so it can be used by boats that do not normally have shore power, without depleting the batteries.

Part 3 - Corrosion Characteristics of Specific Metals Used in Wood Boat Construction

Stainless Steel

The stainless steels that are usually used in sea water are the austenitic, or 300 series, which are alloys of iron, chromium, and nickel. Their rate of simple electrochemical corrosion in seawater is negligibly small, but they are susceptible to two particular types of localized corrosion called **pitting** and **crevice corrosion**. The 18-8 stainless steel alloys like the common Type 304 (18-8 refers to the percentage chromium and nickel contents) are rendered corrosion-resistant by an adherent oxide film called the **passive film** that forms and is maintained on the metal surface in the presence of oxygen. A deficiency of dissolved oxygen in the electrolyte can allow the passive film to break down without immediate self-repair. Chloride ions can also break down the passive film. In either case, the corrosion usually takes the form of small but deep pits. Open-surface pitting is initiated by chlorides and only occurs in salty electrolytes. Crevice corrosion is initiated by low oxygen levels and it may occur in salty or non-salty electrolytes, but chlorides definitely aggravate it. Pitting and crevice corrosion are particularly damaging in the case of tanks or tubes which have relatively thin walls, and where a very small total amount of corrosion can cause failure by penetrating the wall.

The low oxygen levels that trigger crevice corrosion usually occur where small volumes of seawater are trapped or cut off from the outside flowing water. Plankton and other small organisms in the water use up much of the available oxygen and they die. Their decomposition consumes even more of the oxygen, resulting in a local body of low-oxygen electrolyte that allows the passive film to deteriorate, which then triggers crevice corrosion. Typical locations for crevice corrosion are under barnacles or other marine growth attached to stainless-steel shafts, the surfaces of stainless steel shafts inside stern tubes where the narrow grooves of the stern bearing allow only limited communication with the outside water, within the grooves of rubber stern or strut bearings, in crevices between propeller hubs and propeller shafts, in screw threads between bolts and nuts, and, important in wood boats, the covered-over heads of stainless-steel fasteners or the shanks of stainless-steel fasteners passing through wet wood.

Open-surface chloride-induced pitting is greatly reduced when the stainless steel contains small amounts of molybdenum. Type 316 stainless-steel is essentially Type 304 with a few percent by weight of molybdenum. The molybdenum also somewhat reduces the tendency for oxygen-deprivation-induced crevice corrosion, but crevice corrosion is still quite common with Type 316 and other alloys with molybdenum.

Crevice corrosion is unpredictable. With copper-alloy wood-hull fasteners the corrosion rate is fairly predictable and is also quite uniform from one fastener to another. However, within a group of stainless-steel fasteners in a wood hull a small number will often be completely destroyed by crevice corrosion while the remainder will be more or less unaffected. This is important to keep in mind when inspecting fasteners. With bronze or steel, all of the fasteners in a given area of the hull will usually be in similar condition, so relatively few samples taken from various areas of the hull will give a fairly accurate picture of the overall condition. With stainless steel, only one or two in ten might be badly corroded, with the others like new, so much larger samples are necessary - it is very easy to randomly miss the bad ones when only sampling a small number.

If you look at the Galvanic Series, you will see that, unlike any other metals on the chart, stainless steels have two separate potentials listed. The passive potential, which is what you generally measure using a reference cell on a large piece of the metal immersed in seawater, is the potential of the stainless steel when the passive film is intact. The passive potential of stainless steel is among the most positive potentials of any commonly used-metal. The active potential is the potential of the metal without the passive film, and it is not too different from the potential of plain carbon steel. The active potential usually exists only in small active areas of any object, and the presence of these active areas will usually not affect the overall potential that one might measure.

Crevice corrosion and pitting are in fact a type of galvanic corrosion between active areas and passive areas (which have much different natural potentials) on the same stainless steel object (or on electrically-connected stainless-steel objects in close proximity). As noted above, the active area is usually very small compared to the passive area, resulting in a galvanic cell with an area ratio tremendously unfavorable to the active areas, and typically, rapid and severe corrosion at the active areas.

Cathodic protection is very effective in preventing open-surface pitting and also at preventing crevice corrosion in fairly shallow crevices. Very deep crevices, such as on the surfaces of prop shafts inside long stern tubes with the entrances partly blocked by stern bearings, are not as amenable to cathodic protection. In the case of stainless-steel shafts inside long shaft tubes, corrosion can be prevented by operating the shaft frequently during periods of wet lay-up or by frequently flushing the water inside the tube to prevent stagnation. Injecting fresh water into such tubes before periods of vessel inactivity can be quite effective.

The guidelines for cathodic protection of stainless steel are different from the standard negative 200mV shift that applies to virtually all other metals. As noted above, stainless steel

usually shows its passive potential when it is measured, because if there are any active areas where pitting or crevice corrosion is proceeding, they are usually so small compared to the rest of the object that they do not contribute measurably to its potential. However, to be assured of full protection it is necessary to shift the potential to the active potential, rather than simply shifting it by -200mV.

The explanation for why stainless steel should be cathodically protected to its active potential is a bit complicated: With any galvanic cell, applying enough cathodic protection to shift the potential of the cell to the natural potential of the cell's anode eliminates the galvanic interaction between the cell's anode and its cathode. However, the anode is still unprotected from simple electrochemical corrosion at its natural potential, so it is necessary to shift the potential of the cell an additional -200mV shift to protect the anode from simple corrosion.

Since crevice corrosion and pitting of stainless steel are, technically, galvanic interactions between the active areas and the passive areas, shifting the potential of stainless steel to the potential of the active areas eliminates the galvanic interactions between the active and passive areas, just as shifting the potential of any galvanic cell to the natural potential of the anode eliminates the galvanic interactions. And, because the simple electrochemical corrosion rate of stainless steel in sea water is virtually zero, eliminating the galvanic interaction between the active and passive areas is all that is necessary to provide full corrosion protection - it is not necessary to go another 200mV more negative than the active potential. So, for 300-series stainless steel, the metal's active potential as listed in the galvanic series is the target potential (and is usually more than adequate) for full cathodic protection.

Copper Alloys

Silicon Bronze

Silicon bronze is an alloy of copper with 1.5% or 3% silicon (Copper alloys C651 and C655). It is one of the most common materials for wood screws, lag and hanger bolts, machine screws, and other bolts used in wood boat hull construction. Silicon bronze has good corrosion-resisting properties. When this material corrodes, it typically wastes away, leaving obvious reduced-diameter sections in the shanks of fasteners.

With year-round immersion in sea water, silicon bronze wood screws of gauge #12 can be expected to last about 20 years and #18 can be expected to last about 35 years. Failure is defined as the point at which the threads are sufficiently corroded that a screw will spin in its hole if an attempt is made to tighten it or to back it out, or the screw will break during withdrawal due to corrosion, or the slot will be too corroded to allow withdrawal. Clearly the holding power is reduced considerably before that point is reached.

Silicon bronze has one major drawback. It is particularly susceptible, among all copper alloys, to a phenomenon called *erosion-corrosion* in flowing water. The protective corrosion-product film that provides much of its corrosion resistance washes away easily in flowing water,

exposing the underlying material repeatedly to further corrosion. So this material is best used where it is buried entirely in the structure. Heads of bolts or screws should be under putty or wood plugs, or at least very well-painted. There have been cases of silicon bronze lag bolts used to secure stainless-steel propeller cages, with the heads of the bolts exposed, that failed within a year or two in the high-velocity environment around the propeller, with the heads of the bolts completely wasted away. Because of the severity and rapidity of this type of corrosion, such cases are often mis-diagnosed as stray-current corrosion or as a galvanic effect of the stainless steel. (In fact, stainless steel and most copper alloys usually get along quite well in sea water, with no serious galvanic interactions).

Brasses

Brasses comprise a number of alloys of copper and zinc. They are strong and relatively inexpensive as copper alloys go, but alloys containing more than about 15% zinc (which includes most of the brasses) are susceptible to a form of corrosion called, in general, *de-alloying* or in particular, in the case of brass, *dezincification*. A dezincified brass fastener or fitting retains its outward appearance and dimensions but its outer layers have converted into a porous, weak, brittle copper. Brass is no longer extensively used as a wood hull fastener material - it was replaced many years ago by silicon bronze. When brass is unintentionally substituted for silicon bronze for hull fasteners, these fasteners often have a very short life. One particular alloy of brass called *naval brass* (Copper alloy C464) contains tin, which inhibits the dezincification to some extent, and it can often give acceptable service in sea water.

Copper-Alloy Castings

The principal copper casting alloys used in wood hulls are leaded red brass (alloy C836) and the manganese “bronzes”, such as alloy C865. C836 is 85% copper, 5% tin, 5% lead, and 5% zinc. This is the material from which most cast sea-water plumbing fittings are made - thru-hulls, seacocks, strainers, etc. It is very corrosion-resistant even in moving sea water, and does not usually require cathodic protection. However, it is quite weak, and it should not be used in a mechanical capacity. Because of this weakness, it is bad practice to use thru-hulls alone to secure seacocks to hulls without also bolting the seacock flanges to the hull independently, and it is particularly bad to hang sea valves from thru-hull stubs protruding through the hull.

Manganese “bronze” (not really bronze, but brass) is a family of very strong high-zinc brass casting alloys. Many bronze propellers are made from Manganese bronze. The weakest alloy of the series, C865, is suitable for underwater hull fittings and usually shows good corrosion resistance even without cathodic protection. The stronger alloys in the family (C861 and C863) are not suitable for underwater use without completely reliable cathodic protection, and they should probably not be used underwater at all. These alloys tend to dezincify rapidly. They are sometimes used successfully for deck hardware.

Nickel-aluminum bronze (Nibral®) is sometimes used for propellers. It is very strong and very corrosion-resistant but it is expensive and it is not as easily cast as the manganese bronzes.

Aluminum

Aluminum is usually not, and generally should not be used for fasteners or hull fittings on wood hulls. Aluminum corrodes readily where it is in contact with wet absorbent materials like wood, and this type of corrosion cannot be prevented by cathodic protection. If used underwater, it requires a level of cathodic protection that would cause cathodic wood damage to any wood with which it makes contact.

Steel

Steel is used to some extent as fasteners on low-cost wood hulls because of its cost advantage over copper-alloys. In the past, when materials represented the largest proportion of the cost of a wood hull, saving money on fastener material could make a significant difference in the total cost. Now with labor the largest proportion of total cost, using a less expensive fastener material has only a slight influence on the total cost. Galvanized- steel fasteners are discussed in detail below.

Steel is also sometimes used for underwater fabrications on wood hulls - skegs, rudders and rudder supports, etc. As long as it is properly coated and properly cathodically protected, steel gives good service underwater. If used near the waterline, cathodic protection is not as effective. Hot-dip galvanizing is generally not used to protect large underwater steel fabrications. The hot-dip galvanizing process creates multiple layers of iron-zinc alloys on the surface of steel. The outer layer is almost pure zinc, and provides sacrificial-anode cathodic protection if the underlying steel is exposed. However, some of the intermediate layers are actually cathodic to steel. While hot-dip galvanizing is very effective for steel in marine atmospheric or occasional submersion, epoxy undercoaters and topcoats in conjunction with cathodic protection provide the best protection for steel that is permanently submerged. Hot-dip galvanizing is used for steel fasteners despite its limitations because there is no better alternative to prevent corrosion of threaded or driven steel fasteners.

Part 4 - Where to look for corrosion of fasteners

Inspectors familiar with steel vessels know that the worst corrosion of hull plating often occurs in the “wind-and-water” area - near the waterline and in the band between the loaded and empty load lines. The folk wisdom is that this is because there’s more oxygen near the water surface and more oxygen promotes more corrosion. In fact, there is usually plenty of oxygen to cause corrosion right down to the keels of most vessels. And if you refer back to the illustration of the Galvanic Cell (Figure 3 above), you will see that the actual consumption of metal does not necessarily occur where the oxygen is - the cathodes are where the oxygen is, the anodes (where the metal actually wastes away) may be, and often are, somewhere else.

The reasons that steel plating corrodes more readily near the waterline are:

- (1). Physical damage to the coatings from ice, floating debris, docks, fenders and camels, and small craft coming alongside
- (2). Alternate exposure to both sunlight and water with changes in loading causes greater extremes of thermal expansion of the plating that can adversely affect coatings
- (3). The somewhat higher average temperature of water near the surface; and,
- (4). (Very importantly) Cathodic protection is completely ineffective in and above the splash zone (which is also where the paint is most likely to be physically damaged); and the effectiveness of cathodic protection is considerably diminished just below the waterline because the cross-section of water available for the necessary ion current flow is restricted by the presence of the water surface.
- (5) The waterline area is typically more distant from cathodic protection anodes than deeper parts of the underbody.

None of the factors noted above apply in any meaningful way to the metal parts of a wood hull. Fasteners in wood hulls corrode most quickly not in the “wind-and-water” area, but in the places where the wood in which they are embedded is the wettest. The first fasteners to check (the ones likely to be in the worst condition) are plank fasteners along keel rabbets, those into the floor timbers and into the heels and lower sections of the frames in the deepest parts of the hull, and planking butt fasteners in the deepest parts of the hull.

Most fastener-related structural problems in wood hulls involve the fasteners that connect the planks to frames, floor timbers, stems, transoms, etc., and fasteners in planking butts. These planking fasteners are usually of smaller diameter than those connecting together components of the structural backbone and major transverse structural members such as floor timbers and frames. Because the rate at which corrosion proceeds from the outside surface of a metal part inward does not depend on fastener diameter, smaller-diameter fasteners reach the point at which their holding power is compromised before larger fasteners do.

Catastrophic hull failures involving plank fasteners virtually always begin at the ends of planks, either where planks fasten to stems, transoms or chines, or plank ends at butts. The loads on the fasteners at plank ends tend to withdraw them. If the ends of a plank are securely fastened, the plank will generally stay in place (barring unusual hull stresses or shock loads) regardless of the condition of the fasteners in the middle of the plank away from the plank ends (which are generally only in loaded in shear). Therefore, during inspections, particular attention should be paid to fasteners at plank ends and butts where a plank can spring away if the fasteners fail.

Galvanized steel fasteners

The corrosion rate of uncoated and unprotected steel in any marine environment is virtually always unacceptable. Galvanizing is the process of coating steel parts with a fairly thick layer of molten zinc that greatly increases the useful life of the steel. Hot-dip galvanizing is done at a high temperature, and it results in the formation of actual metallic chemical bonds between the steel substrate and successive layers of iron/zinc alloys with increasingly high zinc content from the metal surface outward. The zinc is quite corrosion resistant in marine environments, so it is usually many years before the coating corrodes away enough to begin to expose the underlying steel. When small areas of the steel do become exposed, the remaining zinc provides cathodic protection to the exposed steel. The corrosion rate of a part such as a fastener is very low while the zinc coating is intact, and remains low as long as the exposed area of underlying steel is small relative to the exposed area of zinc. The corrosion rate of the zinc accelerates as it begins to act as a sacrificial anode for greater amounts of exposed steel, and when the zinc is significantly depleted, the corrosion rate of the now-uncoated and unprotected steel accelerates dramatically.

Galvanized steel nails often have a surprisingly long useful life, in large part because there are no restrictions on the thickness of the zinc coating on a nail. Threaded galvanized-steel fasteners like wood screws, lag screws, hex-head bolts and carriage bolts, however, tend not to be as long-lasting as nails, since they must be given a much thinner layer of zinc in order not to fill up their threads and/or slots. All galvanized fasteners are subject to installation damage, from hammering on the heads of bolts and nails and from the scraping effects of screwdrivers and wrenches on the slots, heads and nuts of screws and bolts. In addition, the quality of the galvanizing (i.e. its thickness and its adhesion to the steel substrate) varies within any class of fastener. Because of all these factors, the lifetime of galvanized fasteners is much harder to predict than are the lifetimes of fasteners of other metals.

The mode of corrosion of galvanized steel fasteners, and the effects of that corrosion on the structure of the hull vary considerably with location relative to the waterline. Steel fasteners in water-saturated wood tend to waste away, with most of the iron going into solution, eventually leaving a more-or-less empty hole in the wood. However, in wood above the waterline, where the moisture content is considerably lower (but not nearly low enough to prevent corrosion entirely) the tendency is for the steel to combine in place with oxygen to form iron oxides - rust. The old adage “an inch of steel makes twelve inches of rust” is quite accurate. The mechanical

wedging effect of this expansion often causes a lot of physical damage to wood components through which the fasteners pass.

Whenever the head of a fastener has better exposure to oxygen than does the shank, that fastener tends to form a small self-contained galvanic cell. This is more evident in galvanized steel fasteners than in other types of fasteners. The oxygen reaching the head forces the cathode reaction (oxygen reduction) to occur there, and the anode reaction (actual dissolution of the metal) occurs in the shank. The result is that the heads of such fasteners are slightly cathodically protected and are usually in much better condition than are the shanks, so inspection of the head (which is generally relatively easy) does not give a good indication of the condition of the shank (which is typically much harder to get at). The difficulty of predicting the condition of a fastener shank from inspection of its head was an important consideration in the requirement for periodic visual inspection of fasteners that was instituted in USCG NVIC 7-95.

A further consequence of the galvanic activity in a single fastener that the wood around the heads of fasteners often suffers cathodic wood damage, a result of the alkaline conditions caused by the hydroxyl ions which are products of the cathode reaction. This process can occur with any metal fastener, but it is usually more damaging when the fasteners are galvanized steel. This damage that occurs to wood around fastener heads is sometimes called “nail-sickness”.

Galvanized steel fasteners are also susceptible to the effects of ions of more noble metals in the wood in which they are embedded. The mechanism of “replacement” or “deposition” corrosion which is described above in the discussion of corrosion theory is usually merely a footnote in discussions of corrosion. However, in the case of galvanized steel fasteners in wood treated with copper-based wood preservatives, it can become important. Any green-colored preservative such as brushed-on green Cuprinol® (the active ingredient of which is copper naphthenate) or pressure-impregnated CCA (chromated copper arsenate) will provide copper ions that will spontaneously plate out as metallic inclusions of copper on the surface of a galvanized steel fastener embedded in the treated wood. In the process, equal numbers of zinc ions will go into solution (this is the “replacement” process). However, the replacement itself is just the beginning and accounts for only a fraction of the total corrosion resulting from this effect. Once the copper inclusions are there on the surface of the zinc coating, they act as cathodes in a galvanic cell, causing accelerated corrosion of the galvanizing and eventually of the underlying steel. The copper inclusions are themselves cathodically protected by the zinc and the steel, and the copper remains in metallic form, clean, and free of corrosion indefinitely. If the metal on which the copper inclusions are deposited is undermined by corrosion, the copper simply re-plates on the new surface underneath. Inspectors should be very suspicious of the condition of galvanized steel fasteners in any wood that has an obvious green tint (indicating treatment with copper-based preservatives). None of the species of wood likely to be used in small-passenger-vessel construction are naturally green-colored.