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"Corrosion Control: Galvanic Corrosion and Stainless Steel"

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Galvanic corrosion is the most frequent cause of unexpected corrosion failures in seawater. It has caused failures of ship fittings and deckhouse structures, fasteners, hull plating, propellers, shafts, valves, condensers, and piping. In sea atmospheres, galvanic corrosion causes failures of roofing, gutters, and car trim. The reason that galvanic corrosion causes so many failures is that it can occur any time that two different metals are in electrical contact in seawater. Since most structures and devices are made of more than one kind of metal, this diversity of materials is common and frequently overlooked in corrosion prevention activities. Let's look at why this type of corrosion happens, and how to identify it.

Metals in seawater corrode by releasing metal ions into the water around them. This happens at different rates for different metals, but in all cases the metal must first lose one or more electrons for it to be able to go into solution in the water. These electrons travel to another part of the wetted metal surface and react with something in the water, usually dissolved oxygen. The balance between the reaction where metal ions go into the water (the anodic reaction) and the reaction that uses up the electrons generated (the cathodic reaction) causes the metal to sit in a specific narrow range of voltages. This voltage range can be measured, and may be different for each metal in each type of water. When the voltages for each metal in a specific type of water such as seawater are all collected into one place, this collection of voltages is called a galvanic series. A galvanic series can be as simple as a list of metals in order of their voltages, or as complicated as a graph with voltage ranges.

The position of a metal in the galvanic series does not say how fast it will corrode, but it does say something about what happens to it if it is electrically connected to another metal in water. Any time metals with different voltages are electrically connected in seawater, a current will want to flow between them until they have the same voltage. This is the way a battery works.

The metal that donates electrons to this current flow, the one that has a more negative voltage to begin with, will have its corrosion rate increased and is called the anode. The other metal, which has a more positive voltage to begin with, receives electrons and will have its corrosion rate reduced. It's called the cathode. The more negative metal anode is said to undergo galvanic corrosion, while the more positive metal cathode is said to experience cathodic protection. So, to prevent galvanic corrosion the metals must either be at the same voltage before they are coupled, not be placed in electrical contact, or not be immersed in an electrically conductive water like seawater.

Designers who want to prevent corrosion usually like to make structures and devices out of corrosion resistant materials. However, they may not consider the interaction between the different materials that they choose. For example, some aluminum alloys do not corrode very fast in seawater, and are used for boat hulls. Some bronze alloys also do not corrode very fast in seawater, and are used for propellers. As long as the propeller does not come in electrical contact with the hull, everything works well. But if the two come in contact through a bearing, gearing, or the boat engine itself, the galvanic series tells us what will happen. The aluminum is very negative compared to the bronze, so the electrical contact will cause the aluminum hull to be an anode and its corrosion rate to increase, causing heavy pitting and eventual failure of the aluminum hull.

The galvanic series tells us that the more negative metal will corrode more quickly when electrically coupled in seawater, but not how fast. Two metals far apart in the series will not necessarily experience

more corrosion than two metals close together. Finding the rate of corrosion in a galvanic couple requires knowledge of polarization, the ability of a metal to change voltage while accepting or giving up a certain amount of electrons. A metal that polarizes easily, that changes voltage quickly with a small amount of current, will not cause much corrosion of metals coupled to it. It also will not have much increase in corrosion when it is the anode in a couple. An example of a metal that polarizes easily in seawater is titanium. Metals that are harder to polarize, such that it is hard to change their voltage when current is applied, will cause or experience a lot of galvanic corrosion, depending on the other metal in the couple. Examples of metals that are hard to polarize include copper alloys and some aluminum alloys. So, a piece of aluminum will corrode faster if it is coupled to hard-to-polarize copper than it will if coupled to easy-to-polarize titanium in seawater, even though the voltage of the titanium is farther away from aluminum than the voltage for copper.

The larger the wetted surface area of the cathode, the worse will be the corrosion on the anode. For example, steel corrosion will be increased by contact with copper, according to the galvanic series. A steel fastener used to hold a copper plate will corrode quickly, because there is a large area of copper and a small area of steel. However, a copper fastener will not cause much increase in corrosion of a steel plate because its area is so small compared to the steel. This effect was first discovered by Sir Humphry Davy when he was exploring attaching copper plates to ship bottoms to prevent barnacle growth. This leads to an interesting rule of thumb: always paint the cathode. To slow down galvanic corrosion on the anode, you can paint the cathode (which is not corroding) to decrease its wetted surface area. Painting the anode will only increase its corrosion rate at defects in the paint.

Recognizing galvanic corrosion is not always easy. If a metal normally corrodes by pitting, it will just pit faster when it's the anode in a galvanic couple. If it normally corrodes uniformly, it will do so more quickly when coupled. So galvanic corrosion can't be recognized by the form the corrosion attack takes. Sometimes galvanic corrosion can be recognized because it is usually worse close to the cathode that is causing it. In the copper fastener case above, the steel will corrode more quickly close to the fastener than far from it. Galvanic corrosion will usually be worse near joints between dissimilar metals. But the best way to recognize galvanic corrosion is to know the order of metals in the galvanic series and look for the more positive metals in the vicinity of the corrosion failure. If they are there, they likely contributed to the problem.

Corrosion of Stainless Steels

Aside from steel, stainless steels are the most common construction metals. There are many different types of stainless steels, divided into five major categories by crystal structure type. The austenitic stainless steel alloys, with AISI numbers from 200 to 399, are usually nonmagnetic. The alloys with numbers of 300 or above contain more nickel than those with numbers below 300, and have better seawater resistance. These 300-series alloys are very corrosion resistant, and are used for architectural applications, boat topside fittings, and household goods such as sinks and silverware. The 300-series alloys will usually show no appreciable corrosion in fresh water or sea atmosphere. The 400-series ferritic and the martensitic alloys are usually magnetic, stronger, and less corrosion resistant than the austenitic alloys. They are used for knife blades and certain hand tools. These alloys will sometimes suffer from mild surface rusting when exposed to fresh water or sea atmosphere. Duplex and precipitation hardenable stainless steels are specialty alloys. Some are very strong and not very corrosion resistant, such as 17-4PH, and others have intermediate strength and corrosion resistance between the austenitic and the ferritic or martensitic alloys. There are some specialty alloys that are very corrosion resistant because they add more special elements to the alloy, and are consequently somewhat more expensive than standard grades, such as the austenitic 6XN.

Stainless steels get their corrosion resistance by the formation of a very thin surface film, called the passive film, which forms on the surface in the presence of oxygen. Therefore, stainless steels usually have poor corrosion resistance in low-oxygen environments, such as under deposits, in mud, or in tight places, called crevices, where structures or hardware are attached. This is particularly true in seawater, where the chlorides from the salt will attack and destroy the passive film faster than it can reform in low oxygen areas. All of the stainless steels except the best of the specialty alloys will suffer from pitting or crevice corrosion when immersed in seawater. One of the best 300-series stainless steels is type 316. Even this alloy will, if unprotected, start corroding under soft washers, in o-ring grooves, or any other tight crevice area in as little as one day, and it is not unusual to have penetration of a tenth of an inch in a crevice area after only 30 days in seawater. If water flows fast past a stainless steel, more oxygen is delivered to the stainless steel and it corrodes less. For this reason, stainless steels have been successfully used for impeller blades and propellers. These need to be protected from corrosion when there is no flow.

Painting stainless steels usually does not stop the crevice corrosion; it will occur any place where there is a scratch or nick in the paint. For this reason, I usually recommend against using any stainless steel except certain specialty alloys in seawater for more than a few hours at a time. There is a strong tendency to use in seawater the same materials that work well in fresh water or sea atmosphere, so that types 303, 304, and 316 stainless steel are often used for undersea applications. They will also usually fail if the exposure is long enough, unless they are in continuous solid electrical contact with a material that will provide them with cathodic protection such as steel or aluminum. As soon as the electrical contact is broken, the steel will corrode.

Crevice corrosion of stainless steels happens irregularly, but when it occurs it is very destructive. For example, if 10 stainless steel screws are put in a plate in seawater, it may be that all but one will be un-attacked, as bright and shiny as the day they were made. That one screw, however, may well have attack over one quarter inch deep in only a few months. The attack will occur in crevices where it can't be seen, and will destroy the screw from the inside out. This is because the corrosion starts inside the crevice between the screw and the metal, where it can't be seen, then proceeds inside the metal where there is no oxygen, sometimes hollowing out the part or giving it the appearance of Swiss cheese.

Even the best of stainless steels may have its corrosion resistance affected by the way it is made. For example, 316 stainless steel is very corrosion resistant in fresh water, but when it is welded, the areas next to the welds experience a thermal cycle that can cause that material to corrode. This is called sensitization, and can lead to the appearance of knife-line attack next to welds. This is why certain heat treatments should be avoided with this and similar alloys. On the other hand, a low-carbon version of 316, called 316L, will not be sensitized, and can be welded with little effect on corrosion properties.

Austenitic stainless steels can suffer from stress corrosion cracking to various degrees when fully immersed in seawater. Stress corrosion cracking is cracking without much metal loss in the presence of a continuous applied load in the environment. If a susceptible material fails by cracking and has numerous side cracks besides the one causing the failure, stress corrosion cracking should be suspected. The ferritic and duplex stainless steels usually do not have this problem.

Questions and Answers

When buying stainless steels, some companies claim that they passivate them. What is passivation, why is it done, and does it make the stainless steel corrode less?

When a stainless steel is passivated, it is put into a bath of an oxidizing acid, such as nitric acid. Stainless steels get their corrosion resistance from the formation of a very thin corrosion product film of uncertain composition called the passive film. It was observed that when stainless steels were first treated with an oxidizing acid, they would later appear to corrode less than if they had not been treated. It was thought that the oxidizing acid somehow thickened the passive film on the stainless steel to make the steel more corrosion resistant. Therefore, the treatment was called passivation. We now know that this treatment doesn't affect the passive film in a way that lasts very long in water. The film will stabilize at the same thickness when exposed to the same water whether or not passivation has been done. Then why do stainless steels appear to corrode less after passivation? The oxidizing acid treatment is essentially a cleaning process that removes small particles of iron and other impurities that have gotten on the surface of the stainless steel during the rolling process, or are in the structure of the stainless steel itself and happen to be protruding from the surface. These particles corrode in waters that normally don't corrode stainless steels, leaving behind rust or other corrosion products that are readily visible. It looks like the stainless steel is corroding when, in fact, it is only the surface particles that corrode. Cleaning these particles off with the acid treatment means that they will not later corrode and leave behind ugly rust spots. It therefore seems that the stainless steel is corroding less. Some people believe that surface particle corrosion can start pitting corrosion, but controlled tests show that pitting will still happen even if all of these particles are removed.

The reason for the passivation treatment now becomes clear. It makes the stainless steel look prettier after it has been exposed to the water for a while. It actually doesn't affect the corrosion of the stainless steel itself, however. The treatment is fairly cheap, and usually doesn't hurt anything, so manufacturers usually go ahead and do it, just to avoid later questions about "rust" spots forming on their stainless steel. Passivation can be a problem for parts with tight crevices that can trap the acid used. Over time, these acids can cause crevice corrosion. For parts without crevices, passivation does have a benefit if the stainless steel is to be given some later treatment for which a clean surface is necessary. For example, it is prudent to use passivation before painting or plating over the stainless steel.

Some divers meticulously rinse their equipment off with fresh water after diving in salt water, and others don't. I haven't seen any problems with my equipment if I forget to rinse it off once in a while. Does this rinsing really do any good?

Yes. The chlorides in salt water cause the stainless steel and aluminum alloys that your equipment is made from to pit or to corrode in crevices where oxygen access is limited (and where, by the way, you can't see it happen until it's too late). When you take your equipment out of the water, oxygen can usually get to all of the crevice areas, which stops any crevice corrosion. However, if a crevice is very deep, trapped saltwater might cause corrosion to continue. Corrosion in these deep crevices will be stopped by a fresh water rinse. Because your equipment is made from a lot of different metals, galvanic corrosion can also be a problem as long as the different metals are covered with salt water. The lower conductivity of fresh water reduces the amount of galvanic corrosion that can occur. Finally, the salt deposits that form when seawater evaporates are not only ugly, but also hygroscopic, that is, they absorb moisture from the air. Salt deposits absorb enough moisture for the surface to become wet when the relative humidity exceeds 50-75 percent. Your equipment will start to corrode when it is sitting in the shed and you think it is dry. This is the same reason why cars in the northeast corrode more than they do in the south. Road salts form a layer on the car that causes the car to corrode every time the relative humidity goes over 50 percent, even sitting in the garage. So, rinse your equipment. Take good care of it, your life depends on it. And while you're at it, take your car to the car wash after you've driven it on salty roads and it will last longer too. **UW**

Dr. Harvey P. Hack, Northrop Grumman Corp., hosts a column on corrosion in each issue of UnderWater. If you have questions, tips, or comments, write to The Corrosion Column, Underwater Magazine, 5222 FM 1960 W, Suite 112, Houston, TX 77069 or email harvey_p_hack@mail.northgrum.com.

GALVANIC CORROSION

Galvanic corrosion occurs when two dissimilar metals are in contact with an electrolyte, which is a medium through which an electrical current can flow. The rate of corrosion depends upon the differences in electrical potential, or anodic-cathodic relationship, of the metals in the joint as defined by the Galvanic Series of Metals & Alloys (see table at right). A highly anodic material in contact with a highly cathodic material will corrode much more quickly than two highly cathodic materials or when the materials used are closer together in the Galvanic Series.

When corrosion does occur, the anodic material is the most likely to corrode, whereas the cathodic material is the least likely to corrode.

To reduce the likelihood of galvanic corrosion in a fastened joint, it is recommended the designer choose materials that are grouped together in the Galvanic Series chart. If that is not possible, other recommendations are: 1) select materials which are as close together in the chart as possible; 2) provide a barrier between the two metals, such as paint, non-metallic washer or gaskets; 3) design the fastener as the cathode so the cathodic area is small as compared to the anodic area; and/or 4) use a metallic finish on the fastener that is close on the chart to the mating material.

Anodic End (Most Likely to Corrode)
Magnesium Magnesium Alloys Zinc
Aluminum 1100 Cadmium Aluminum 2024-T4 Steel or Iron Cast Iron Chromium-Iron (active) Ni-Resist Cast Iron
Type 304 Stainless (active) Type 316 Stainless (active)
Lead-Tin Solders Lead Tin
Nickel (active) Inconel Nickel-Chromium Alloy (active) Hastelloy Alloy C (active)
Brasses Copper Bronzes Copper-Nickel Alloy Monel Nickel-Copper Alloy
Silver Solder Nickel (passive) Inconel Nickel-Chromium Alloy (passive)
Chromium-Iron (passive) Type 304 Stainless Steel (passive) Type 316 Stainless Steel (passive) Hastelloy Alloy C (passive)
Silver Titanium Graphite Gold Platinum
Cathodic (Least Likely to Corrode)