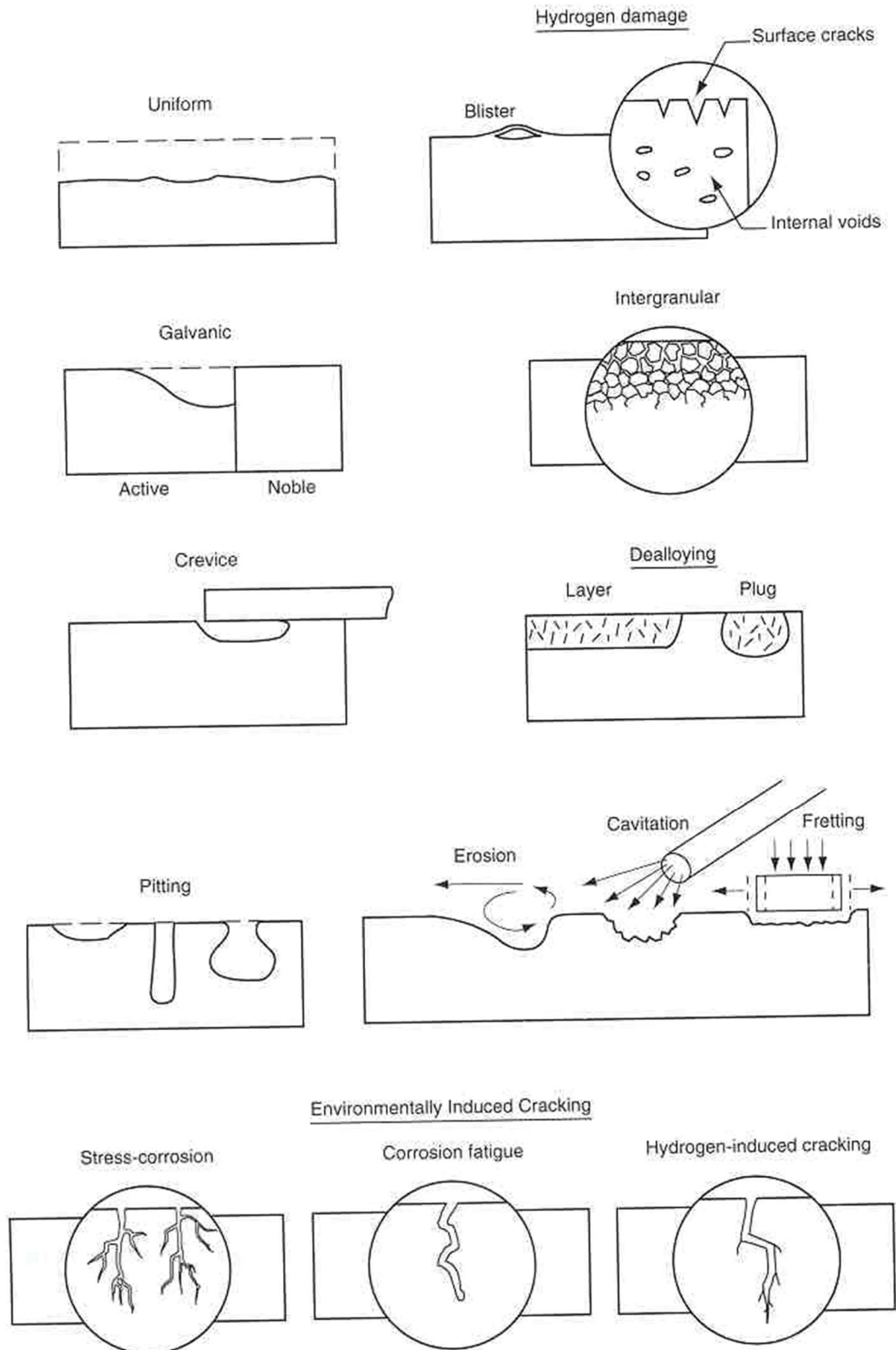


## **CHAPTER 5**

### **CORROSION TYPES**

- 5.1 Uniform Corrosion
- 5.2 Galvanic Corrosion
- 5.3 Crevice Corrosion
- 5.4 Pitting Corrosion
- 5.5 Other Localized Corrosion
- 5.6 Selective Leaching aka Dealloying
- 5.7 Erosion-Corrosion
- 5.8 Stress-Corrosion-Cracking (S.C.C.)
- 5.9 Intergranular Corrosion
- 5.10 Fretting
- 5.11 Biological corrosion
- 5.12 Stray current corrosion

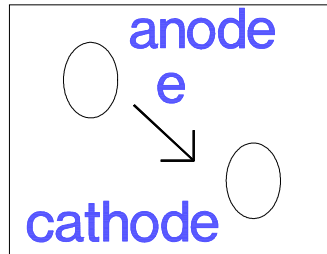
The diagram on the following page illustrates the main types of corrosion which will be discussed in this chapter.



Corrosion types [from Jones (1996)].

## 5.1 Uniform Corrosion

This corrosion results from the continual shifting of anode and cathode regions of the surface of a metal in contact with the electrolyte and leads to a nearly uniform corrosive attack on the entire surface. An example of such corrosion is the rusting of steel plate in seawater.



If the rate of metal loss is known, allowances can be made in design and maintenance to accommodate the corrosion. Although it is termed uniform corrosion, it is characterized by the average surface loss.



Uniform corrosion of storage tanks [from Jones (1996)].

## 5.2 Galvanic Corrosion

When two different metals are exposed to a corrosive environment, an electrical potential difference will exist. If the two metals are electrically connected, the more active metal will become the anode in the resulting galvanic cell and its corrosion will be increased. An example of such a corrosion cell is the use of steel bolts to hold copper plates together

Not all galvanic corrosion is detrimental. Zinc coated steel, or galvanizing, is used to protect steel, not because the steel is resistant to corrosion, but because the zinc, being anodic to the steel, corrodes preferentially. Hence, the steel is protected cathodically by making any exposed areas of steel into cathodes.

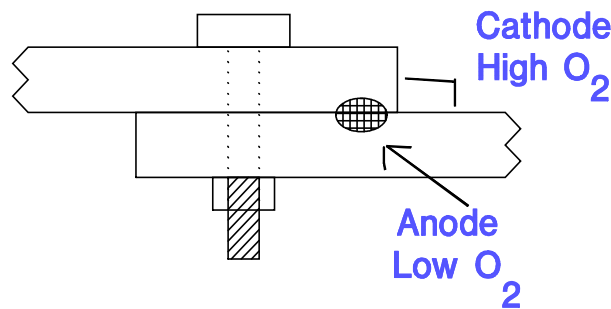
It is generally good practice not to use dissimilar metals unless it is necessary, but if it is, the following precautions should be used:

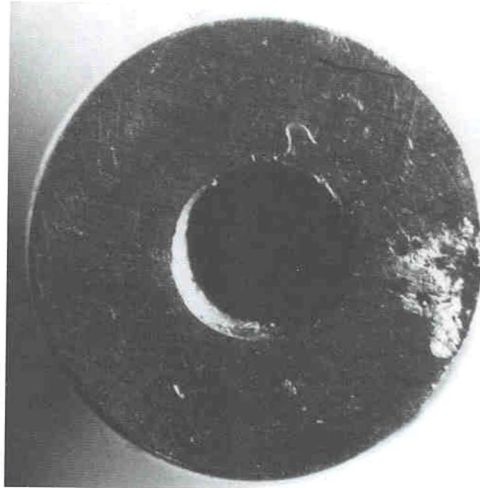
- Attempt to electrically isolate the metals.
- Use protective coatings on the metal surface(s), generally the cathode
- Cathodically protect the less noble metal.
- Put corrosion inhibitors into the system.
- Use design in which anodic part may be replaced easily.
- Keep out moisture.
- Use metals that are close to one another in the galvanic series.
- Design so that the anode/cathode area ratio is high.
- Use design allowances to account for the corrosion.

### 5.3 Crevice Corrosion

Crevice corrosion is a localized attack which occurs when crevices, formed by lapped joints, or areas of partial shielding, are exposed to corrosive environments. Such resulting cells are referred to as concentration cells. Two common cases are oxygen cells and metal-ion cells.

Oxygen concentration cells occur when the shielded area becomes depleted in oxygen and the area acts as an anode relative to the oxide region. As illustrated in Figure 24, the corrosion becomes quite rapid because of the small shielded area as compared to the unshielded area. Do not get confused with the concentration polarization that we previously discussed. In the case of an oxygen cell, we have an oxygen "gradient" that forces the formation of the anode and cathodes with respect to the oxygen levels.

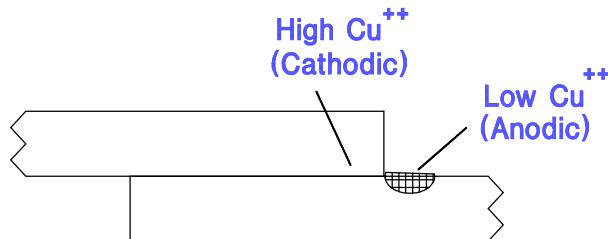




Crevice corrosion of stainless steel [from Jones (1996)].

The initial driving force of such corrosion is the oxygen cell. The continued growth is fostered by the accumulation (often caused by the same factors that produced the low oxygen level) of acidic, hydrolyzed salts within the crevice. Alloys, such as 18-8 stainless steels, are subject to oxygen cell crevice corrosion.

Metal-ion cells are formed mainly with copper alloys. The shielded area accumulates corrosion products and becomes cathodic to the regions outside of the crevice where corrosion products are kept washed away. The figure below illustrates this type of concentration cell.



Another example of metal-ion cell corrosion occurs when relative speeds of electrolyte over the metal surface are greater at one point than at another, thus resulting in metal-ion crevice corrosion. A good example is where a disc of metal is rotating at high speed in seawater. Corrosion occurs near the edge where linear velocities ( $v=\omega r$ ) are the highest and the metal-ion concentration is low (since the ions are repeatedly swept away). The high velocity, higher than in regions closer to the hub of the disc, sweeps away the metal-ions, thus forming anode regions. At the center of the disc, where velocities are lower, the metal acts as a cathode and is protected (Do not confuse this with the discussion on "immunity" from corrosion where the low ion concentration was one of the entering arguments. That was an equilibrium concentration. In this case, metal ions continue to form because we can't reach an equilibrium concentration).

However, the two concentration cells corrode at different regions of the crevice. The oxygen cell corrodes under the shielded area while the metal-ion cell corrodes outside of the area. As stated before, the initial driving force behind the corrosion is either the oxygen or the metal-ion cell. Its continued growth is governed by the accumulation of corrosion products, clacareous deposits, and salts within the crevice.

## 5.4 Pitting Corrosion

Pitting is an extremely localized attack that eventually results in holes in the metal. It is one of the most destructive and insidious forms of corrosion. Basically, the alloys subject to pitting are those that rely on an oxide film for protection, such as stainless steels. The initiation of a pit can be the result of any of the following:

- a) Chemical attack, such as ferrous chloride or aerated seawater on stainless steel.
- b) Mechanical attack such as an impact or scratching that removes small areas of the protective film.
- c) Crevice corrosion resulting from tiny deposits on the surface, especially in stagnant seawater.

Some theories state that pitting is just a special case of crevice corrosion.



Localized pitting of stainless steel [from Jones (1996)].

## 5.5 Other Localized Corrosion

In addition to the pitting and the crevice corrosion, the following are also localized corrosion:

- Poulitce corrosion - attack which occurs at the edge of a damp fabric.
- Deposition corrosion - corrosion process in which a more noble metal deposits on a less noble metal and causes attack due to a bimetallic cell. It is common in copper/aluminum systems
- Filiform corrosion - localized attack of a metal surface beneath a coating due to oxygen concentration cells.

## 5.6 Selective Leaching aka Dealloying

Selective Leaching corrosion results from areas of a metal surface being different metallurgically from other, adjacent areas. Brass, for example, is an alloy with zinc and copper in a "solid solution". It can corrode with the zinc being selectively removed from the alloy, leaving behind the copper. It makes the alloy porous and compromises its mechanical properties. In brass it may be identified when its yellow natural color turns reddish or coppery in appearance. It is helpful to add a small amount of tin to the alloy to prevent dealloying.

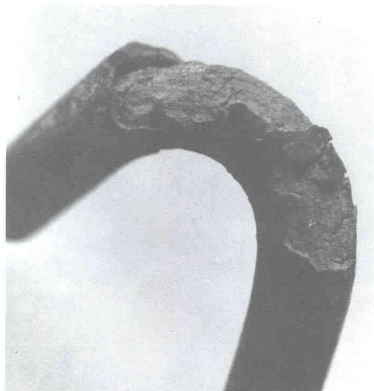
Such selective leaching is known as "dezincification". Cast irons can corrode in such a manner that the iron is selectively corroded away, leaving behind a soft graphite layer. This is referred to as "graphitization". Other examples are referred to as dealuminification, denickelification, decobaltification, etc. where the terms refer to the metallic element that is selectively corroded away.

The mechanism of selective leaching has been explained as follows for a brass alloy:

- A. the brass corrodes
- B. the zinc ions stay in solution
- C. the copper plates back on as a solid layer

The problem with this theory is that the corrosion occurs even under high electrolyte flow velocities when one would surmise that the copper ion would be swept away before they could plate out.

A second theory, again for brass, is that the zinc corrodes preferentially, leaving behind copper in a lattice structure. A corrosion process in which the less noble metal in an alloy is attacked preferentially and replaced in the matrix by cathodic products. The most common example of this occurs with brass and is termed dezincification. In the dezincification of brass, the zinc in the alloy's matrix is attacked and copper remains.



Dealloying of brass [from Jones (1996)].

## 5.7 Erosion-Corrosion

Erosion-Corrosion results from a high velocity electrolyte flow whose abrasive action accelerates the corrosion. This corrosion is especially severe when the electrolyte contains solids in suspension. The effect is to remove a protective oxide from the film surface, thus exposing fresh alloy to corrode. Erosion-Corrosion could be thought of as pitting on a much larger scale.

There is, in fact, a limit to what electrolyte velocities can be tolerated by specific metals. Copper-nickel alloys are selected for seawater service based on their resistance to erosion-corrosion (amongst other requirements). This table illustrates these limitations.

### Recommended Maximum Velocity to Reduce Impingement/Velocity Effects in Seawater

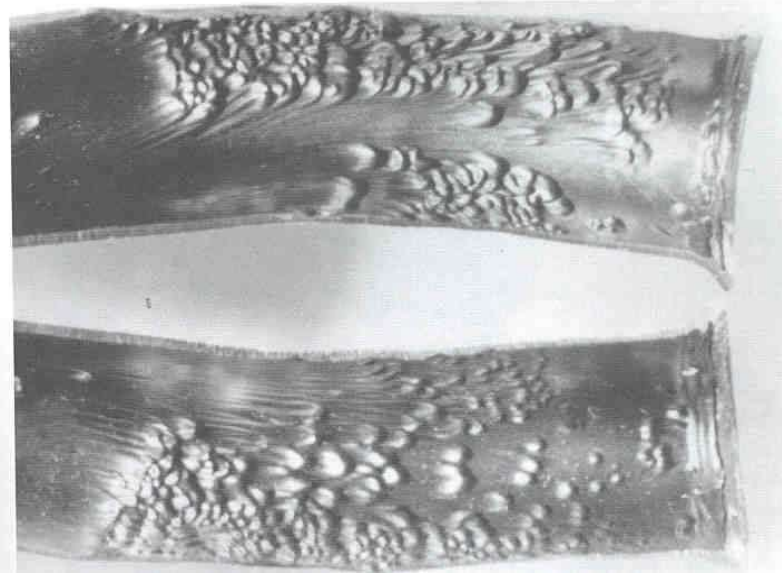
<u>Alloys</u>	<u>Maximum velocity, fps</u>
<u>Copper</u>	3
90 Cu/10 Ni (with 1.25% Fe)	12
70 Cu/30 Ni (with .5% Fe)	15
85 Cu/15 Ni (with .5% Cr)	>15
<u>Titanium</u>	>15

In addition to Erosion, other forms of attack related to velocity effects are:

- Cavitation - the deterioration of a surface caused by the sudden formation and collapse of bubbles and voids due to the turbulence in the liquid. It is generally marked by a pitted or rough metal surface.
- Impingement attack - localized corrosion caused by turbulence or impinging flow. Generally there is a critical velocity below which no impingement occurs and above which attack increases rapidly.

It should be stated that in many cases these three corrosion processes occur simultaneously.





Erosion corrosion [from Jones (1996)].

### 5.8 Stress-Corrosion-Cracking (S.C.C.)

Stress-corrosion-cracking occurs with specific alloys under the following threshold conditions:

- a) Specific corrosive environment solution composition
- b) Minimum tensile stress levels
- c) Temperature
- d) Metal composition
- e) Metal structure

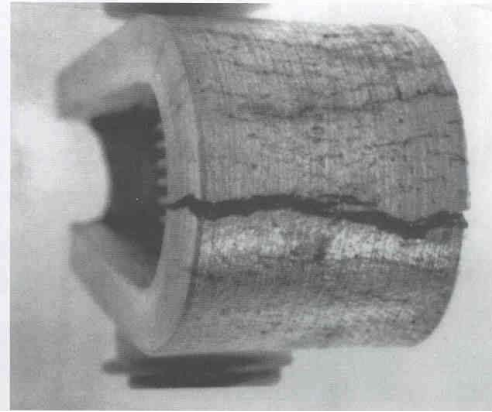
Some examples of scc are the brass and stainless steel alloys. Specific brass alloys will crack in ammonia containing environments when a minimum threshold tensile stress is reached. Stainless steel alloys do not crack in ammonia environments, but will crack in chloride solutions.

The interplay of the conditions leading to scc is not well understood. It is believed that the corrosion causes a pit or surface discontinuity to form on the metal which then functions to act as a stress concentrator. The presence of a minimum threshold tensile stress, coupled with the corrosion, causes the crack to propagate. Additionally, during the initial corrosion, the tensile stresses could cause the protective films on the surface to rupture, thereby exposing the metal to the corrosive environment.

This particularly dangerous corrosion type can be the result of environmental factors or cyclic stresses. The following are the major types of cracking attack:

- Corrosion fatigue - the accelerated failure of a metal which undergoes cyclic loading due to its presence in a corrosive environment.
- Stress corrosion cracking (SCC) - the corrosion induced cracking which occurs in alloys under high tensile stress. The cracks start on the surface and go inward. It should be noted that the stress can be the result of cold working, forming, or external loading.

- Hydrogen embrittlement - the loss in ductility of a metal due to the saturation of atomic hydrogen in the grain boundaries. It occurs at local cathodic sites and is aggravated by stress and compounds such as hydrogen sulfide.
- Liquid metal cracking - metals subjected to simultaneous tensile stress and certain molten metals can undergo this type of cracking. It is most common in mercury/copper alloy systems.



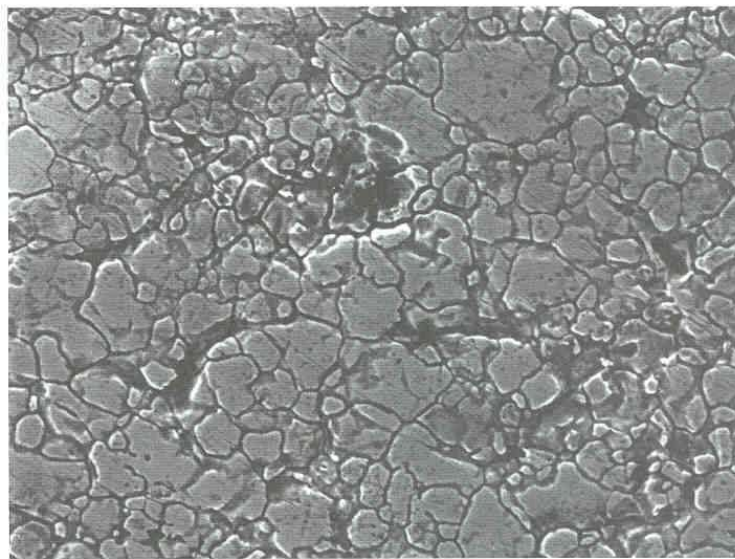
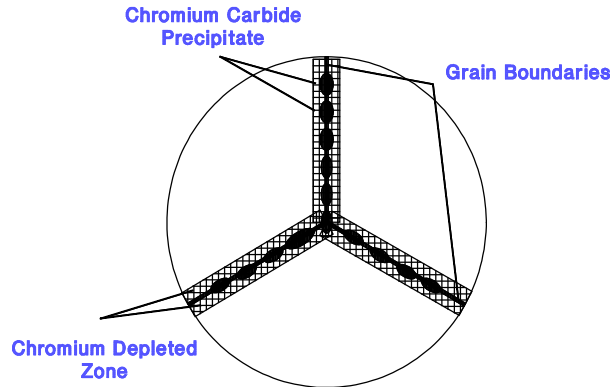
Stress corrosion cracking [from Jones (1996)].

## 5.9 Intergranular Corrosion

On a microscopic level, metals and their alloys have small, distinguishable regions called grains. Within an individual grain the orientation of the atomic arrangement (called a lattice) is the same. Individual grains have different orientations and the boundary between the grains is called the grain boundary. Normally, grain boundaries are no more reactive in corrosion than the grain itself. Under certain conditions, however, the grain boundaries are altered from the grain itself by impurities and/or enrichment (or depletion) of one of the alloying elements.

Heat treatment and welding can lead to changes in metal composition which may incite intergranular corrosion. In severe cases, intergranular corrosion can lead to a marked decrease in mechanical properties and can, in extreme cases, turn the metal into a pile of individual grains.

One of the most common examples of intergranular corrosion occurs in stainless steels. During welding of the alloy, or heating in the temperature range of 950°F to 1450°F, the alloy becomes sensitized or susceptible to intergranular corrosion as illustrated in Figure 26. The chromium carbide ( $\text{Cr}_{23}\text{C}_6$ ) is not soluble in this temperature range and precipitates out of the grain into the grain boundary. As a result, the area of the grain adjacent to the grain boundary is depleted of the chromium and becomes anodic to the rest of the grain and to the grain boundary. The corrosion of this depleted grain boundary area is very severe and occurs in environments and acids where the alloy would not normally corrode. The simplest solution to the stainless steel intergranular corrosion problem is to cast alloys with carbon contents below 0.03%. (This prevents the formation of the chromium carbide and the chromium stays in solution).



Intergranular attack [from Jones (1996)].

### 5.10 Fretting

A rapid localized attack which occurs on mated surfaces under load when a small amount of slip is allowed to occur. It is often observed on bearings, shafts, and gears in mounted in vibrating machinery. Not only is mechanical damage of the surface possible, but the protective surface film of the metal is also removed. This in turn hastens electrochemical corrosion processes.

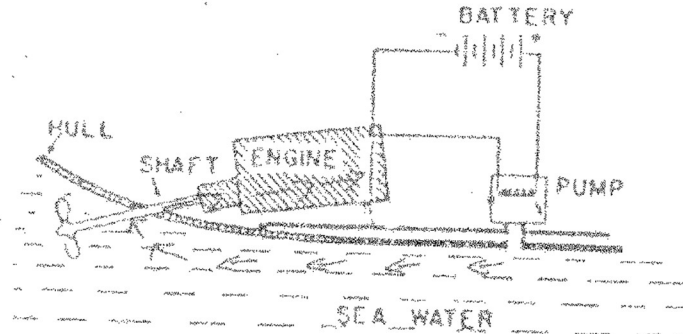
### 5.11 Biological corrosion

Biological organisms can play a major role in metal attack. This attack is usually categorized in the following two headings:

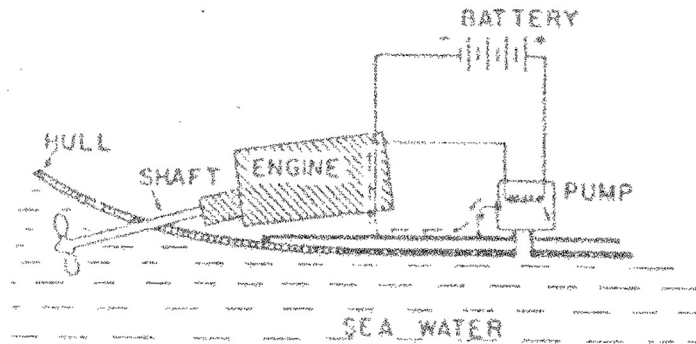
- Microbially induced corrosion (MIC) - aerobic and anaerobic bacteria and other microorganisms contain enzymes and can produce metabolites which accelerate corrosion. This can manifest itself in pitting type corrosion of the metal surface.
- Macrofouling effects - barnacles, oysters, and other macrofoulers produce by-products that are often acidic and can accelerate corrosion. These organisms also create crevices at their attachment points that can lead to crevice corrosion.

### 5.12 Stray current corrosion

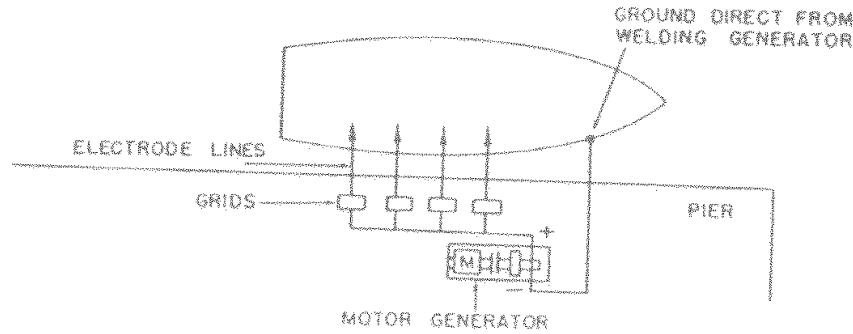
Corrosion can be accelerated by the action of electrical currents entering a metal from some external source such as a generator or a battery and leaving the metal to continue its flow in whole or part through the seawater electrolyte. As an example of stray current corrosion, consider the bilge pump illustrated below. The electrical connections were made such that the current found a path from the pump and its through-hull connection to the seawater and back through the propeller shaft and engine to the battery.



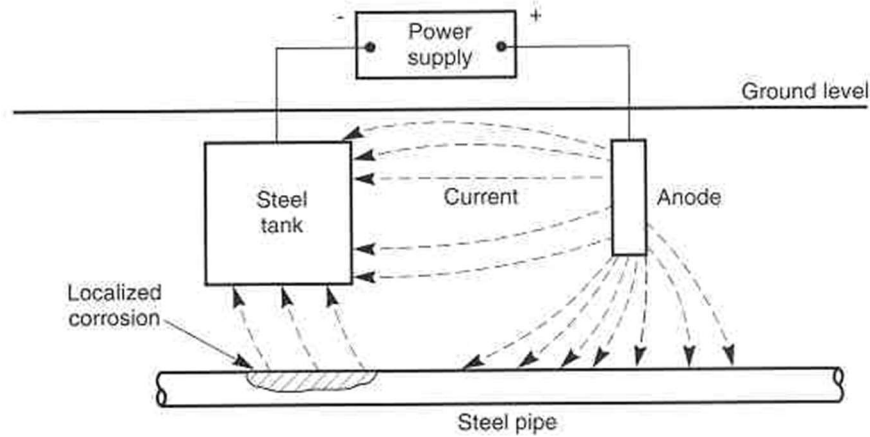
To prevent such corrosion, all metal surfaces exposed to bilge water or projecting through the hull should be electrically connected (bonded) to the negative side of the battery as shown in the following figure:



Another example of stray current corrosion damage to a ship is through the use of an onshore welding generator below. If the return leads to the onshore generator do not have ample current carrying capacity, some of the current will find its way back through discontinuities in the paint on the submerged hull, resulting in corrosion of the hull. To avoid such corrosion, the generator should have been placed on the ship's deck and its AC lines could have been run from shore. Any AC stray current to shore would have caused little damage.



Stray current corrosion can also occur when the current from a cathodic protection system passes from the anode to a metal object which was not designed to be protected before going to the object which was intended to be protected. The result can be severe local attack on the unprotected metal where the current exits. It can also attenuate the current to a point that the object to be protected is underprotected.



Stray current corrosion [from Jones (1996)].

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