Biocorrosion
This chapter considers the issue of biofilm based bacterial assisted corrosion (i.e. biocorrosion) of metals submerged in the marine environment. Through water channels within the biofilm, the thriving bacterial colony is able to absorb nutrients and oxygen from the water. However, as growth continues and the depth of the slime layer increases, there is little penetration of oxygen in the layers against the pipe or vessel surface. Anaerobic bacteria can propagate in the deeper layers of the biofilm where little oxygen reaches. Some of these anaerobes are capable of metabolizing carbon from stainless steel, and some produce nitric, sulfuric, or other organic acids that further accelerate corrosion. The depletion of oxygen in the wetted surfaces under bacterial colonies can result in the formation of "differential aeration cells" that can lead to galvanic corrosion. For information on the course can be found at the following website: http://www2.hawaii.edu/~mcooney/oest740/.
1. Biocorrosion

Corrosion

Most metals in their refined form (except for a few noble metals such as gold) are inherently unstable. The tendency of refined metals to revert to their natural mineral states is a driving force behind corrosion processes. There are a number of different types of corrosion, including:

1. **General or overall corrosion**: a uniform attack over the entire exposed area of a surface across a wide range of temperatures.
2. **Pitting corrosion**: High-localized corrosion rates with little or no general corrosion to the areas surrounding the pits.
3. **Galvanic corrosion**: when two dissimilar metals are electrically connected in the presence of an electrolyte, the more electrochemically active metal corrodes by giving up electrons and corrodes at an increased rate.
4. **Microbiologically induced corrosion (MIC)**: Microorganisms form colonies on surfaces, leading to corrosive conditions.
5. **Stress-corrosion cracking (SCC)**: when a stressed metal is exposed to certain types of environments it may become susceptible to stress-corrosion cracking at stress levels that may be significantly below the yield strength of the material.

Corrosion specifically refers to any process involving the deterioration or degradation of metal components (http://www.corrosion.doctors.org). It is an electrochemical process consisting of two half reactions: an **anodic** reaction involving the oxidation (ionization) of the metal and a **cathodic** reaction involving the reduction of a chemical species in contact with the metal surface. **Oxidation** is loss of electrons while **reduction** is the gain of electrons. The electrons produced by the anodic half reaction will need to be consumed by a cathodic half reaction in relatively close proximity to the corrosion reaction. Corrosion is the sum of these two half reactions, that is the anodic reaction of the metal dissolving as ions and generating, in the process, free electrons, and the consumption of these free electrons in a secondary process termed the cathodic reaction. Both reactions are needed to balance charge and complete the electric circuit.

When metal atoms are exposed to an environment containing water molecules, they can give up electrons, becoming themselves positively charged ions. This is shown in Figure 1A. Pure metals and/or their mixtures (alloys) are in a thermodynamically unstable state and the process of
oxidation (i.e. the metal losing electrons) moves the metal to a more thermodynamically stable state with an accompanying loss of energy (in the form of free electrons) to the environment. The free electrons will react with adjacent reactant molecules to form oxidation by-products that will (in the absence of microbes) for an “oxidative layer” adherent to the metal that slows the rate of oxidation because the oxidative layer (an oxide/hydride layer) that serves as a diffusion layer to other reactant molecules [1].

The steps are presented in Figure 1. In this case hydrogen ions from water dissociation can migrate to the metal surface and react with the two electrons to form hydrogen gas, which will then form a thin “polarizing” film that will inhibit further corrosion by eliminating the water to metal contact. Dissolved oxygen, however, in the water will react with the hydrogen to reform water and therefore breakdown the thin film, which will permit the corrosion reaction to continue. Any agent that reduces the effect of the polarizing film is called a depolarizing agent.

Atmospheric corrosion
Corrosion is an electrochemical process requiring an electrolyte. Condensed water is the electrolyte in air corrosion. Metals exposed to the atmosphere can, if the air is sufficiently humid (above 60%), be covered in a thin invisible liquid film containing water and air that serves as the electrolyte. Under these conditions all the elements necessary for corrosion are present: a metal to support the anodic reaction, water and oxygen to support the cathodic reaction. In this reaction the metal is the oxidant (or molecule that is oxidized and provide the electrons) while oxygen acts
as the reductant, or the molecule that accepts the electrons and gains the electrons in the process. Corrosion processes exposed to air are generally rather slow as the oxidation products adhere to the surface and create, in the process, an oxide/hydroxide layer that serves as a diffusion barrier to the other reactants [1].

\[
\begin{align*}
\text{Anode half reaction:} & & 2M \rightarrow 2M^{2+} + 4e^- \\
\text{Cathode half reaction:} & & O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \\
\end{align*}
\]

**Biocorrosion**

Often termed microbiologically influenced corrosion (MIC), biocorrosion refers to corrosion that is influenced by the presence and activities of microorganisms and their metabolites. In biocorrosion, organisms living in association with the metal surface influence either half reaction through their mere presence on the surface and their ability to carry out specific biochemical reactions that alter the physical/chemical conditions at the metal surface. *MIC does not involve a new mechanism of corrosion.* Rather, the roles of the microbes are to consistently create surface conditions that favor the maintenance of cathodic and/or anodic reactions [1]. The mechanisms potentially involved in microbial influenced corrosion are:
• Cathodic depolarization, whereby the cathodic rate limiting step is accelerated by the microbiological reaction.

• Formation of occluded surface cells, whereby microorganisms form “patchy” surface colonies. Sticky polymers attract and aggregate biological and non-biological species to produce crevices and concentration cells, accelerating attack.

• Fixing of anodic reaction sites, whereby microbiological surface colonies lead to the formation of corrosion pits, driven by microbial activity and associated with the location of these colonies.

• Underdeposit acid attack, whereby corrosive attack is accelerated by acid final products of MIC “community metabolism”, principally short-chain fatty acids.

Microorganisms associated with corrosion damaged are classified as:

• Anaerobic bacteria that produce highly corrosive species as part of their metabolism.

• Aerobic bacteria that produce corrosive mineral species.

• Fungi that may produce corrosive by products in their metabolism, such as organic acids.

• Slime formers that may produce concentration corrosion cells on surfaces.

The bacteria involved in metal corrosion have frequently been grouped by their metabolic demand for different respiratory substrates (i.e. electron acceptors). The capability of many microorganisms to substitute alternative oxidizable compounds in place of oxygen as terminal electron acceptors under anaerobic conditions accentuates their capacity to sustain conditions conducive for corrosion of metals [1]. Also, the capacity for bacteria to produce corrosive metabolic by-products makes them a real threat to the stability of metals. For the most part, no single species of bacteria are associated with corrosion. Typically they exist in synergistic communities that effect electrochemical processes through cooperative metabolism. The bacteria that are associated in these types of communities include sulfate-reducing bacteria, sulfur-oxidizing bacteria, iron-oxidizing/reducing bacteria, manganese-oxidizing bacteria, and bacteria secreting organic...
acids and exopolymers or slime [1]. Their activity often occurs in biofilms and tends to pit the iron [2].

As much as 20% of corrosion to metals and nonmetals result from microbial activity. One of the most significant is the corrosion of iron or steel, for instance in oil technology, underwater pipes, offshore platforms, and on any equipment item exposed to marine water. The primary reaction is the dissolution of iron.

\[ Fe \leftrightarrow Fe^{2+} + 2e^- \]

In principle, this reaction can be performed by a number of oxidants (compounds that accept the electrons). In the atmosphere, the oxidant is the oxygen molecule, which causes rust. In the presence of water, under anaerobic conditions, the presence of protons (H\(^+\)) from water yields hydrogen (H\(_2\)). Such anaerobic corrosion of iron (Fe) is frequently linked to the activity of sulphate-reducing bacteria (SRB) [2], especially the Desulfovibrio species due to their capacity to consume hydrogen effectively. A good example can be found with the sulfate reducing bacterium, Desulfovibrio desulfuricans, whose role is to reduce the hydrogen gas that forms as a result of the cathodic reaction of iron with water (Figure 3).
Despite their identity as the main culprits of anaerobic corrosion, the underlying mechanisms remain complex and insufficiently understood [2]. They are also relatively slow, presumably because in this scenario the protons must first absorb to the metal surface, accept the electrons and form hydrogen in the process, and then return to the aqueous phase.

\[ 2e^- + 2H^+ \rightarrow 2H_{\text{absorbed}} \]

\[ 2H_{\text{absorbed}} \rightarrow H_2(\text{absorbed}) \]

\[ H_2(\text{absorbed}) \rightarrow H_2(\text{aqueous}) \]

It is presumed that the combination of the H atoms is the rate-limiting step [2]. Biofilm based sulphate-reducing bacteria, however, promote the anaerobic oxidation of iron. Without the action of the bacterium the hydrogen gas layer would build up and minimize the water-metal contact and thus reducing the corrosion rate. In this manner, the bacterium is a “depolarizing agent” because it catalyzes the reversible oxidation of hydrogen. In this direct mechanism, SRB stimulate the corrosion process by scavenging the free cathodic hydrogen (or the hydrogen film) on water-exposed iron [2]. The electron removal (from the system) as a result of hydrogen utilization forces more iron to be dissolved at the anode. More the hydrogen sulphphide produced by the bacterium binds out the iron in a stable complex (iron sulphphide) and thus acts as a corrosive agent.

Recently, a novel marine corrosive sulphate-reducing Desulfobacterium-like isolate has been reported that that reduces sulphate (in the presence of iron) much more rapidly than conventional hydrogen scavenging Desulfovibrio species, suggesting that the novel surface-attached cell type obtained electrons from metallic iron in a more direct manner than from the free hydrogen normally presumed be the carrier [2] (Figure 4). In the same paper, they reported the isolation of Methanobacterium-like archaeon species that produced iron in the presence of methane much faster than known methanogens (which convert the hydrogen to methane instead of H2S as do the Desulfovibrio species), again suggesting a more rapid access to the electrons than via hydrogen.
production [2]. Because of the speed of sulphate reduction by the isolated strains the authors supposed that some mechanism other than consumption of the chemically formed hydrogen must occur [2].

To explain this phenomenon, the authors proposed a direct electron uptake via cell surface associated redox-active components, possibly a cytochrome [2]. Specifically, that the electrons are directly taken up through an electron transport system that both produces sulphate reduction enzymes and, through contact with hydrogenase enzyme, produces hydrogen H\(_2\).

\[ Fe \rightarrow \text{electron\_transport\_system} \rightarrow \text{sulphate\_reduction\_enzymes} \]

\[ \uparrow\downarrow \]

Hydrogenase \(\rightarrow\) H\(_2\)

Figure 4
Slime producing bacteria

Virtually all non-sterile surfaces submerged in an aqueous milieu accumulate an attached microbial population [1]. The developed biofilms consist of microbial cells, their extracellular polymeric substances (EPS) consisting of complex mixture of cell-derived polysaccharides, proteins, lipids, and nucleic acids, and inorganic precipitates derived from the bulk aqueous phase or corrosion products of the metal substratum. Microorganisms that produce copious quantities of EPS during growth have been implicated in localized attack on stainless steel. Oxygen consumption by the microbial cells within the biofilm reduces the oxygen concentration at the metal surface to an extent that the protective oxide film cannot be reformed where cracks have breached a protective oxide film. In other cases, the presence of EPS has been suggested to protect metal surfaces from corrosion. In these tests, a microbial consortium of *Bacillus sp.* and *Deleya marina* produced a metal binding EPS that reduced the rate of corrosion of carbon steel [1]. Reports vary and are contradictory, but biofilm forming microorganisms recovered from sites of corrosion on stainless steel include *Clostridium ssp.*, *Flavobacterium ssp.*, *Bacillus ssp.*, *Desulfivibrio ssp.*, and *Pseudomonas ssp.*

References