

CORROSION IN SEAWATER - BIOLOGICAL EFFECTS

E. Bardal

Norwegian University of Science and Technology, Norway

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Summary

This section deals with a review of the electrochemical behavior of metallic materials in

seawater, the formation of biological films and the effect of these films on the corrosion characteristics.

As a background for the main sections, elementary electrochemical concepts of corrosion in aerated solutions are described at first, including potential - current density diagrams and the mechanism of crevice corrosion.

The formation and growth of biofilms, macroorganisms and inorganic deposits, the effects of various conditions on film formation, and the biological content and activity of biofilms are summarized. Also some interactions between the biofilm and inorganic deposits produced under free corrosion or cathodic polarization are included.

A brief presentation of corrosion behavior of various materials in seawater is given, with particular emphasis on biological effects. Materials dealt with are structural steels, copper and copper alloys, stainless steels, nickel alloys and titanium.

The behavior of usually corrosion-resistant materials has been dealt with in more detail. Particularly the behavior of stainless steels is described with some comparison with copper and nickel alloys and titanium. The most critical effect of biofilms on stainless steels is the strong increase of cathodic efficiency, i.e. depolarization of the oxygen reduction reaction and the consequent ennoblement of the corrosion potential (open circuit potential) in natural seawater below 30 to 40°C. The relationship between the observed cathodic depolarization and the content of the biofilm as well as proposed mechanisms of the effect of the biofilm on the oxygen reduction are reviewed.

This effect will in many instances increase the liability to crevice corrosion initiation, making steels like AISI 304 and 316 unsuitable for service in natural seawater environment. Because of the biologically induced cathodic depolarization, crevice corrosion rates are also strongly increased. Similar effects are found to various extents on galvanic corrosion rates on less noble materials, i.e. copper and copper alloys, steels and aluminum alloys, coupled to stainless steels or titanium. Moreover, the biofilm effect leads to higher current demand for cathodic protection of stainless steels.

The most common method to prevent marine growth and biological effects on stainless steels in seawater is the use of chlorination. Various effects of chlorination are described in this context. Continuous chlorination results in a higher potential than in untreated seawater and increases the crevice corrosion initiation liability further. This can be avoided by intermittent chlorination, which is possible to control automatically by means of electrochemical monitoring. Stainless steels in chlorinated seawater can be effectively protected by resistor controlled cathodic protection (RCP).

1. Introduction

Seawater is commonly used as feed for desalination processes. Extensive use is made of stainless steels and copper base alloys in the intake systems and heat rejection sections of thermal processes such as Multi-Stage Flash and Multi-Effect Desalination. The content of this article is relevant to both natural and chlorinated seawater which provide

the corrosive environment in these parts of the process. Later in these processes, increases in temperature and deaeration destroy the bacterial activity, which the article describes, and provide a different and less corrosive environment (Todd, 1997).

In the case of membrane processes such as reverse osmosis (RO), the seawater feed may be chlorinated but is not normally deaerated. Two types of membrane are in common use, namely cellulose acetate and polyamides. The latter is very sensitive to oxidants in the seawater and dechlorination is needed to avoid rapid membrane degradation. This can lead to biological fouling as microorganisms which are not destroyed by chlorination are able to colonize and grow on the membrane surface. Although no data are available for RO systems on the microorganisms which stimulate the cathodic reaction as described in this article, it would be prudent to assume that they also can grow in such systems and stimulate corrosion on stainless steels, which are normally used for high pressure components (Todd, 1997).

For many engineering materials, seawater is known to be the most corrosive of all natural elements. The corrosivity depends on various factors. Of primary interest is the content of oxygen, since the dominating cathodic reaction in the corrosion process is the reduction of oxygen. This reduction reaction may be strongly affected by the presence of microorganisms, which therefore constitute one of the most important factors. The effects of the microorganisms are particularly strong on some materials which are usually considered as corrosion-resistant, such as conventional stainless steels, e.g. the AISI 304 and 316 types, and Ni-Cu-alloys. In some cases the effects may be rather dramatic, and lead to unpleasant and expensive surprises for users of these materials.

Research carried out during the last two decades on stainless steels and other corrosion-resistant materials in natural seawater has shown that the detrimental effects are due to the formation of a micro-biological film (a biofilm) on the surface. This film affects the local corrosion initiation tendency as well as the propagation rate at temperatures below 30-40°C. The effects of the biofilm depend much on other factors, particularly the existence of crevices and deposits on the surface, welds and the quality of welding, aeration, periods of exposure in seawater and flow conditions.

In many cases the corrosion-resistant materials are in metallic contact with carbon steel, which protects the more noble materials. The reason for the absence of corrosion on conventional stainless steels in such cases is not always understood. Therefore, for some seawater applications, conventional stainless steels may have a more positive reputation than what is reasonably based on their own properties.

The growth of the biofilm is often prevented by chlorination. The tendency to initiation of local corrosion may increase by this treatment, but the propagation rate of corrosion is typically less in chlorinated than in natural seawater.

Cu-alloys are strongly affected by the environmental conditions. Water velocity is important, and the alloys are sensitive to pollution of the water. Both these factors influence the microbial effects.

The main objective of this article is to describe in detail the interactions between

biological activity and corrosion. The description makes use of corrosion theory concepts such as the relationship between electrode potential and electric currents, and the nature of pitting and crevice corrosion. A short review of the basic electrochemical concepts is therefore presented in the next section.

2. Electrochemical Corrosion

2.1. Electrochemical Corrosion of an Active Material in an Aerated Solution

Figure 1 is a schematic picture of corrosion of a metal M in an aqueous solution containing oxygen (aerated). The corrosion process consists of an anodic and a cathodic reaction. The anodic reaction is oxidation of metal M to metal ions M^{2+} i.e. dissolution of metal, while the cathodic reaction is reduction of oxygen. There is always a transport of charge, an electric current through the interface between the metal and the solution at each of the electrodes (anode and cathode). This process creates an electric circuit without accumulation of charges anywhere. This means that the current passing the interface at the anode, the anodic current I_a , must equal the current at the cathode, the cathodic current I_c .

The rate of current of each electrode reaction depends on the electrode potential. Usually this is expressed in a potential - log current-diagram (E vs. log I diagram) or a potential-log current density diagram (E vs. log i diagram).

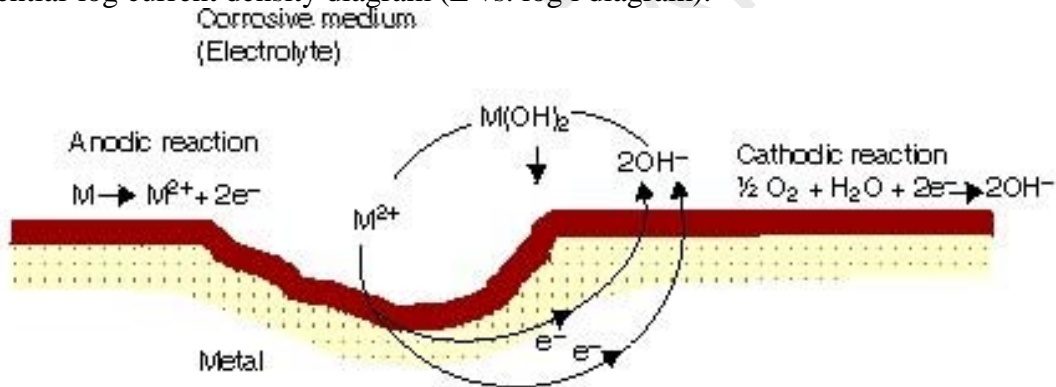
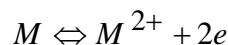


Figure 1. Wet (electrochemical) corrosion of a divalent metal M in an electrolyte containing oxygen.

An E vs. log I diagram for the electrode reactions in Figure 1 is shown in Figure 2. An active metal is assumed in this case, i.e., the anodic reaction is not hindered by a passivating film on the surface.

At the potential E_{oa} the reaction



is in equilibrium, and the potential is named the equilibrium potential or the reversible potential of this reaction. The reversible potential is determined by the thermodynamics of the reaction. The oxidation rate of the reaction equals the reduction at this potential

value. This rate can be expressed in terms of current density, which is the exchange current density, generally denoted i_o , and in our case i_{oa} . For a certain electrode area there is an exchange current I_o . In the case shown in Figure 2 we have an exchange current I_{oa} as a basis for our anodic reaction. Similarly we have the equilibrium potential E_{oc} and the exchange current I_{oc} , for the oxygen reaction. When the electrode potential of the M/M^{2+} reaction is more positive than the equilibrium potential E_{oa} there is a net reaction rate in anodic direction, and this rate increases with increasing potential distance from the equilibrium. The total anodic current depends on the potential as shown by the lower curve, the anodic overvoltage curve. The overvoltage η at an arbitrary potential E is $\eta = E - E_{oa}$.

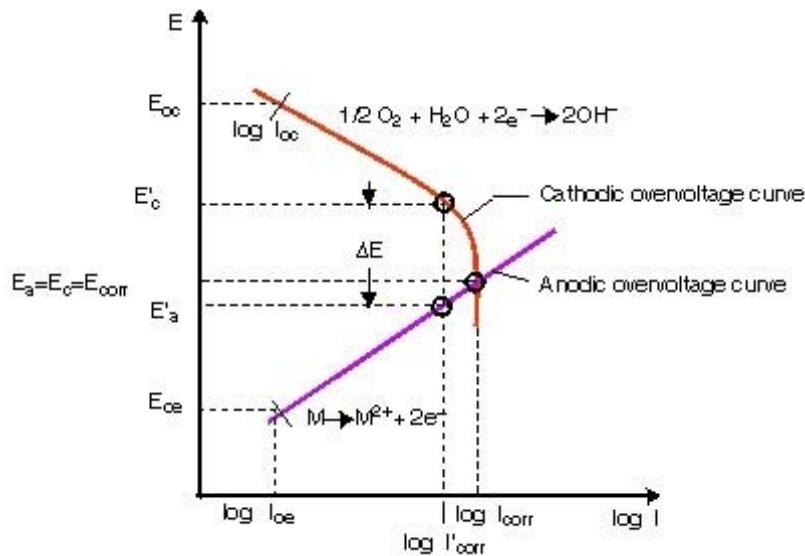


Figure 2. Potential-log current diagram for an active metal corroding in an aerated aqueous solution.

The cathodic reaction increases with decreasing potential (with increasingly negative potential) as illustrated by the upper curve, the cathodic overvoltage curve.

As already mentioned, the anodic current must equal the cathodic current for a metal under free corrosion, $I_a = I_c$. If we assume that there is practically no ohmic potential drop between the anode and cathode, neither in the liquid nor in the metal, the electrode potentials at the anode and the cathode are equal too, i.e. $E_a = E_c$.

These two conditions, $I_a = I_c$ and $E_a = E_c$, are satisfied only at one point in Figure 2, namely at the intersection point between the anodic and the cathodic overvoltage curve. This point defines both the corrosion potential (open circuit potential, rest potential) E_{corr} and the corrosion current I_{corr} . This is the so-called mixed potential theory, which is extremely important for the understanding of corrosion behaviour.

If there is a potential drop ΔE in the electrolyte between the cathode and the anode, the mixed potential theory has to be modified, as illustrated by the dotted line in Figure 2. Now the anode potential E'_a is more negative than the cathode potential

$$E'_c, (E'_c - E'_a = \Delta E).$$

The anodic and cathodic currents are still equal ($= I'_{\text{corr}}$), but lower than in the case of no potential drop in the solution.

The vertical part of the cathodic curve is caused by concentration polarization. Here, the cathodic reaction rate and the cathodic current are limited by the transport of oxygen to the electrode surface. Since the oxygen molecule has no electric charge, the oxygen transfer rate, and thus the cathodic current, is independent of the potential in this potential region. With the corrosion potential located to this region, mass transfer, or diffusion, of oxygen to the metal surface is the rate-determining step in the corrosion process. In other words, the corrosion rate is mass transfer controlled or diffusion controlled.

2.2. Behaviour of Active - Passive Materials

As mentioned above, the situation in Figure 2 represents corroding metals that are active in the whole potential range in question. However, as is well known, many of the corrosion-resistant materials, typically stainless steels, are passive due to an oxide film on the surface. This oxide film prevents the anodic reaction. The potential range where the metal or alloy is passive depends on several factors, of which pH, chloride concentration and temperature are of particular importance. Schematic anodic overvoltage curves for an active-passive material at different pH values and chloride concentrations are shown in Figure 3. In chloride solutions, pitting corrosion occurs when the potential is above a certain critical potential, the pitting potential E_p , which is characteristic for the actual material-environment combination.

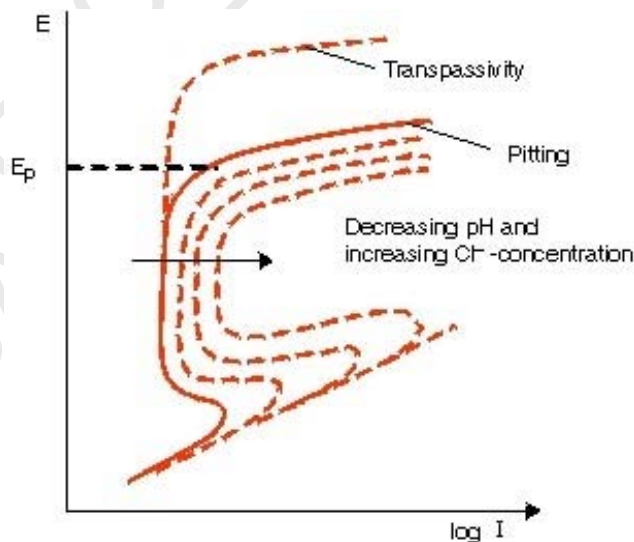


Figure 3. Schematic anodic overvoltage curves for an active-passive metal or alloy. Effects of pH and chloride concentration $E_p =$ pitting potential.

A pit is initiated as a result of very local breakdown of the oxide. Aggressive species

like Cl⁻ ions play an important role in this process. They are adsorbed on the surface and assumed to penetrate the oxide, preferably at sites with oxide defects or weak points. Small anodes and pits are formed at these points. When a pit has been formed, it grows by a mechanism similar to that of crevice corrosion propagation (see next section).

As a result of the reactions, the electrolyte in the pit becomes acidic and more aggressive, which in turn accelerates the corrosion process (autocatalytic process).

In Figure 4 it is shown by anodic and cathodic overvoltage curves how a stable passive state (1) may be established in certain neutral solutions, while pitting may occur in a solution with higher Cl⁻ concentration and/or lower pH, or possibly at a higher temperature (state 2).

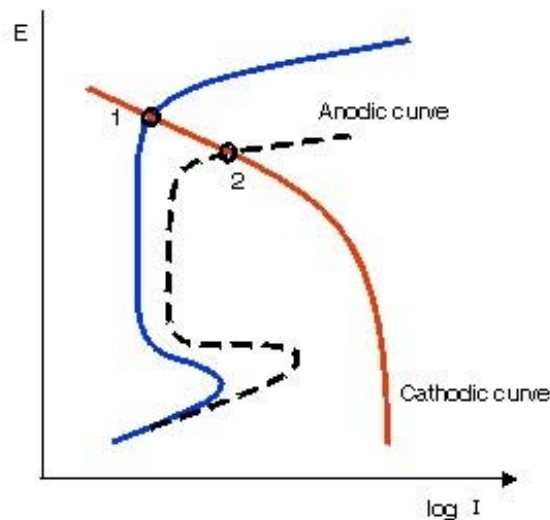


Figure 4. Anodic and cathodic overvoltage curves resulting in a stable passive state (1) in a neutral solution, and pitting (2) at lower pH and higher Cl⁻ concentration.

The experimentally determined pitting potential depends more or less on the test procedure. These data are therefore not exact corrosion characteristics, but they indicate the potential levels at which pitting can be expected.

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