

pH AT POLARIZED METAL SURFACES: THEORY, MEASUREMENT AND IMPLICATIONS FOR MIC

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ABSTRACT

Microorganisms growing on water immersed metal surfaces change the local dissolved oxygen concentration due to microbial respiration. Areas of oxygen depletion are anodic relative to surrounding areas. The pH at these areas decreases due to hydrolysis of metal ions. This process was simulated using linear anodic polarization procedure in the two oxygenated media - 3.5% sodium chloride and 3.5% artificial sea water. Current density and surface pH were monitored in function of applied potential using 304 SS and copper. Surface pH strongly depended both on the kind of metal and water chemistry. Anodic polarization decreased the metal surface pH below 1 creating unfavorable conditions for microbial activity. The results support hypothesis that the microbial colonization of metal surfaces contributes to corrosion only in the early stages of Microbially Induced Corrosion.

INTRODUCTION

The pH at the water surface is influenced by the kind of microorganisms colonizing the surface, their metabolic activity, kind of the metal used, chemical constituents of the water (buffering capacity) and hydrodynamic conditions around the metal sample. Microorganisms growing on water immersed metal surfaces change the local dissolved oxygen concentration due to microbial respiration. Areas of oxygen depletion are anodic relative to surrounding areas. Microbial action cause local anodic dissolution. This process separates anodic and cathodic sites at the metal surface and initiates corrosion. It has been demonstrated (Franklin et al., 1990) that microbial colonization fixes anodic and cathodic places at the metal surface.

The metal dissolves at anodic sites forming ions. The metal ions, hydrolysed by water, form thermodynamically stable metal hydroxides and hydrogen ions H^+ .



A decrease in pH is the direct result of hydrolysis of metallic ions released by anodic dissolution. The solubility of metal hydroxides in water is limited so the pH at the metal surface depends upon the equilibrium constant for hydrolysis. Because of tht the kind of the metal influences the surface pH. Both theoretical and experimental works confirm that surface pH during anodic polarization is very low. Little et al. (1987) calculated that pH at the microbially colonized metal surface can, in some cases be as low as 0.6. The pH change at anodes in localized corrosion of 316L stainless steel in 0.5N NaCl solution has been investigated by Suzuki et al. (1973). They have reported that the pH within a pit to be 0.06-0.17. In addition to the effect of hydrolysis, Suzuki et al. also considered a formation of

hydrochloro-complexes of cations of the dissolved metal and highly concentrated chloride solution to be other processes leading to a decrease in pH. Pourbaix (1976) predicted the pH in pits on copper for solutions containing Cl^- to be 3.5 while the pH of the bulk solutions was 8. The acidification within the pit was explained by hydrolysis of CuCl ($2\text{CuCl} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{Cl}^-$).

This work evaluates the chemical conditions at the metal surface during anodic polarization. The assumption is that the major impact at the metal surface conditions is caused by the local anodic dissolution due to microbial colonization. We neglect other factors as, for example, the presence of extracellular bacterial polymer. This simplification permits us to use the linear anodic polarization of metal coupons to reconstruct the conditions at the metal surface. A direct metal surface pH measurement was used to describe these conditions.

MATERIALS AND METHODS

Measurements were conducted in a 1 liter volume Princeton Applied Research Corporation (PARC) flask equipped with two graphite counter electrodes, a saturated calomel reference electrode (SCE) and a working electrode. Copper and an Allegheny Ludlum 6X (AL6X) stainless steel coupons were used as working electrodes. The pH at the metal surface was measured by a microelectrode positioned at the surface of the working electrode using a micromanipulator. The construction of the microelectrode and the details of the pH measurements are described elsewhere (Lewandowski et al. 1989). Applied polarization potential was changing from +300 mV to -1V (SCE) in case of stainless steel and from +300 mV to -600 mV (SCE) in case of copper. Scan rate was 1 mV/s. The polarization potential was changed using a PARC 273 Potentiostat - Glavanostat. The working electrodes were rinsed with acetone prior to mounting in the PARC flat electrode holder. Measurements of pH were made against standard Ag/AgCl electrode. During the measurements the reactor liquid was purged with air. Measurements were conducted in 3.5% artificial sea water (Instant Ocean) and 3.5% sodium chloride.

RESULTS

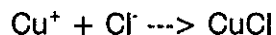
Surface pH of stainless steel during anodic polarization

Surface pH and current density of the 316 stainless steel during anodic polarization in 3.5% artificial seawater and 3.5% NaCl solution are shown in Figures 1 and 2. In general an increase in anodic current density is associated with a decrease of surface pH. There are significant differences in surface pH in the two electrolytes. The current density increases dramatically after the applied potential exceeds the pitting potential (400 mV) in 3.5% NaCl solution. In the case of 3.5% artificial seawater, the surface pH remains constant even the applied potential exceeds the pitting potential (500 mV vs. SCE) and finally decreases rapidly at potential 900 mV vs SCE. This can be explained by the difference in buffering capacities of these two solutions. The bicarbonate present in the artificial seawater neutralized H^+ produced by hydrolysed metal ions. Metal surface pH for applied potential +800 mV(SCE) in sodium chloride was below 1 while in artificial sea water the same applied potential decreased pH to 5. The surface pH of 316 stainless steel is controlled by the metal dissolution rate and buffer capacity of electrolyte.

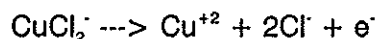
Surface pH of copper during anodic polarization

Surface pH and current density of copper during anodic polarization in 3.5% artificial seawater and 3.5% NaCl solution are shown in Figures 3 and 4. In both electrolytes two

anodic peaks were observed. It has been demonstrated (Giuliani et al., 1971) that the first anodic peak is due to formation of the CuCl film according to the following reactions,



In the first anodic peak region, the cupric ion is not involved in the reaction but the copper is dissolving as the cuprous ion (Lush and Carr, 1979). Hydrolysis of cuprous ion to form cuprous oxide and hydrogen ion caused the decrease of pH in the ascending part of the peak. This can be further illustrated by the E-pH stability diagram of Cu in Cl⁻-containing solution (Figure 5). It results from Figure 5 that for pH around 7 the stable phase is Cu₂O. For pH lower than 5.2 the CuCl is stable. Indeed, the initial formation of CuCl is observed at potential 0 mV (SCE) even for the bulk pH equal 8. The formation of an oxy-chloride complex layer causes the current drop abruptly which, in turn, increases the surface pH due to the decrease of dissolution of copper. Reaction for the second anodic peak is not clear but hypothetically it may be as follows:



It is possible that at the ascending part of second anodic peak, CuCl film reacts with chloride ions to form cuprous chloride complex (CuCl₂⁻) at the surface of the film. The breakdown of CuCl increases the dissolution of copper to cuprous ion and cause pH to decrease again. The cuprous complex will (1) diffuse to the bulk solution, and (2) oxidize to form Cu⁺². Hydrolysis of Cu⁺² and CuCl₂⁻ cause a further decrease of pH after the second anodic peak. The presence of bicarbonate ions causes lower current density obtained in the passive region with 3.5% artificial seawater, and the higher current density obtained with 3.5% NaCl solution. Metal surface pH in this system, however, depends to a much smaller degree on the buffering capacity than in the case of stainless steel. The reason for this may be a reaction between copper and bicarbonate. The surface pH decreased below 1 for +600mV (SCE) applied potential both in 3.5% NaCl and 3.5% Instant Ocean.

CONCLUSIONS

Both systems, stainless steel and copper presented surface pH below 1 when polarized at high anodic potential. The microbial colonization of metal surfaces creates conditions which may initiate corrosion process. Initial presence of microorganisms helps establishing local anodic and cathodic cells. Once the corrosion process is established the conditions for microbial growth deteriorate dramatically. The conditions at the interface between the metal and corrosion products deteriorate because of low pH, high concentration of metal ions and resistance to nutrient transport due to corrosion product accumulation. It can hardly be expected that the microorganisms would demonstrate considerable activity at pH close to zero and in the presence of metal ions. The conclusions support the models assuming that microorganisms only initiate the corrosion process by forming local anodic sites. They also agree well with experimental observations that bacteria on coupons with heavy pitting corrosion are colonizing the edges of the corrosion products next to the bulk fluid (Pope et al. 1990).

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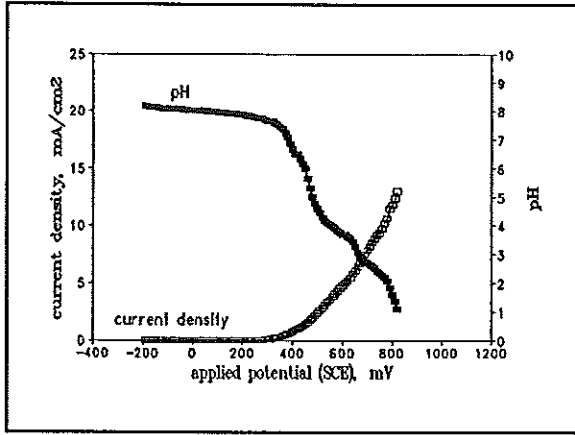


Figure 1 Stainless Steel in 3.5% NaCl

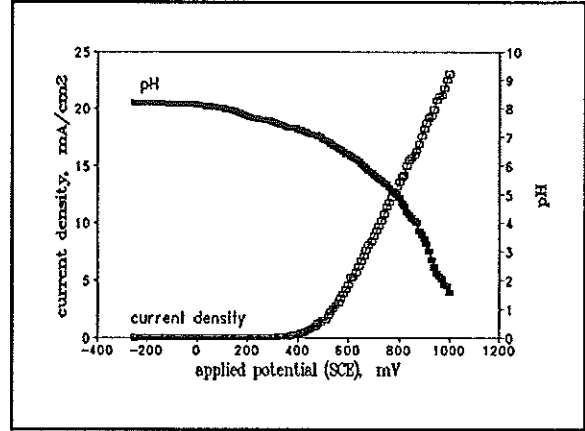


Figure 2 Stainless Steel in 3.5% Instant Ocean

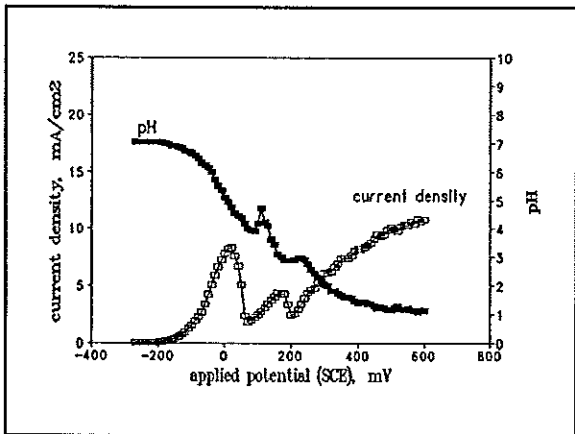


Figure 3 Copper in 3.5% NaCl

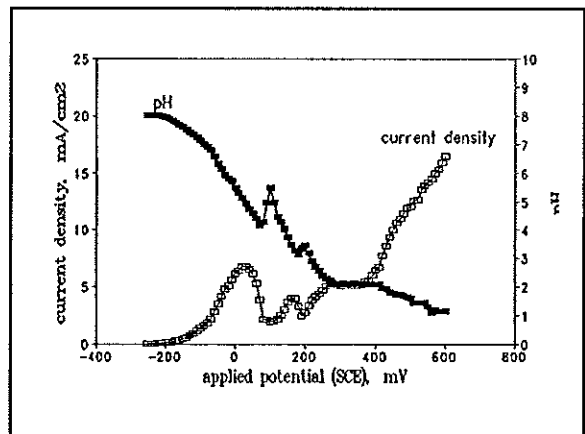


Figure 4 Copper in 3.5% Instant Ocean

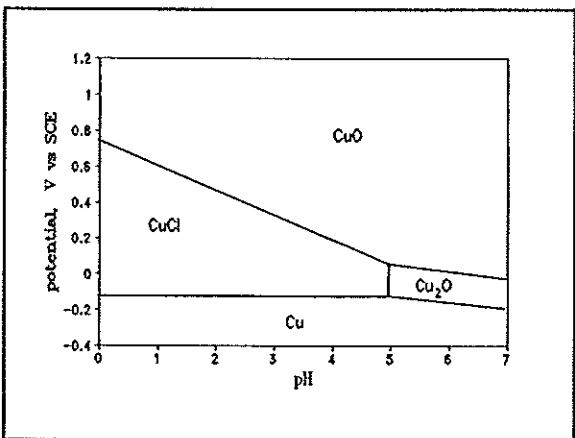


Figure 5 E-pH diagram for Cu in 3% NaCl (Giuliani et al. 1971)

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