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Microbiologically Influenced Corrosion in Copper and Nickel Seawater Piping Systems

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ABSTRACT

Copper and nickel seawater piping systems were severely pitted after exposure to marine and estuarine waters. Surfaces were uniformly covered with thick deposits, ranging in color from blue-green to reddish-brown to black. Pits developed under surface deposits containing 10^4 – 10^5 cm^{-2} sulfate-reducing bacteria in association with other bacteria. Pits were irregular in shape, lacking a consistent morphology. The observed corrosion was attributed to the presence and activities of microorganisms that resulted in differential aeration cells, large cathode:anode surface ratios, concentration of chlorides, development of acidity within pits, and reactions of the base metals with microbiologically produced sulfides. Chlorine and sulfur reacted selectively with iron and nickel in the alloys, leaving copper-rich spongy pit interiors.

INTRODUCTION

Copper and nickel alloys have a long history of successful application in the marine environment. Predominantly copper alloys are frequently used for seawater piping systems and heat exchangers due to good corrosion resistance combined with mechanical workability, excellent electrical and thermal conductivity, ease of soldering and brazing, and a resistance to macrofouling. In oxygenated seawater a film of cuprous oxide, cuprite (Cu_2O), forms on the metal (North and Pryor, 1970). Copper ions and electrons pass through the film. Copper ions dissolve in the water and precipitate as $\text{Cu}_2(\text{OH})_3\text{Cl}$ independent of alloy chemistry (Pollard et al., 1989). Figure 1 presents a set of reactions consistent with observed corrosion behavior for copper alloys in seawater and fresh water. Alloying nickel and iron into copper alters the corrosion product and improves corrosion resistance. The mechanism is not fully understood but appears to be related to control of the cathodic rather than the anodic reaction (Hack et al., 1986). An alloy containing 88.5 percent copper, 10 percent nickel, and 1.5 percent iron has been shown to be the most corrosion resistant copper-based alloy for seawater service (Bates and Popplewell, 1975).

Predominantly nickel alloys have been used extensively in highly aerated fast-moving seawater environ-

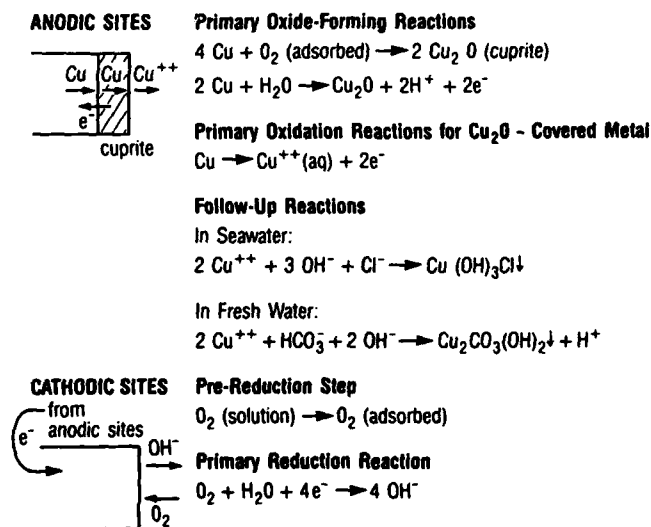


Figure 1. Typical cathodic and anodic reactions on copper alloys in oxygenated seawater and fresh water.

ments, such as evaporators, heat exchanger pumps and valves, diffusers for steam nozzles in steam ejectors, and turbine blades (Tipton and Kain, 1980). Friend (1980) reported that a passive film similar in structure to that observed on pure nickel is formed on Ni-Cu alloys containing more than 30 percent Ni. A metal protected by a passive film is resistant to uniform corrosion. Alloys containing less than this amount of Ni behave like copper. The formation of the protective passive film in nickel is aided by the presence of iron, aluminum, and silicon (Shreir, 1977a).

Copper and nickel alloys are susceptible to several types of localized corrosion. Premature corrosion failures in predominantly copper alloys have been attributed to erosion corrosion caused by the removal or breakdown of the protective film by mechanical forces, such as local turbulence or impingement (Bates and Popplewell, 1975; Shreir, 1977a; Sato and Nagata, 1978) and under-deposit corrosion (LaQue, 1975). In high velocity seawater, predominantly nickel alloys are superior to copper-rich alloys because the protective surface film remains intact under highly turbulent and erosive condi-

tions (Fink and Boyd, 1972). Nickel alloys are susceptible to pitting and crevice corrosion attack under stagnant conditions (Maylor, 1978; Southwell and Alexander, 1967; Stover, 1961).

Both copper and nickel alloys are vulnerable to microbiologically influenced corrosion. Differential aeration (Pope, 1985), selective leaching (Alanis et al., 1986), under-deposit corrosion (Pope, 1986), and cathodic depolarization (Miller, 1970) have been reported as mechanisms for microbiologically influenced corrosion of copper and nickel alloys. Differential aeration occurs when the concentration of oxygen is higher at an area of the metal surface and lower at surrounding areas. In oxygenated electrolytes, areas that are lower in oxygen concentration will be the anodes of the differential aeration cell while surrounding areas will be cathodes. Differential aeration cells frequently form in association with surface deposits. As is the case with other chemical reactions, corrosion tends to reach an equilibrium rate lower than the initial rate as a result of the formation of anodic and cathodic reaction products. For example, the cathodic reaction would slow down if the hydrogen product of the cathodic reaction were not removed. The decreased reaction rate is due to "cathodic polarization." Any reactant that can remove the cathodic reaction product is a cathodic depolarizer. Pope et al. (1984) have proposed that the following microbial products accelerate localized attack: CO_2 , H_2S , NH_3 , organic and inorganic acids; metabolites that act as depolarizers; and sulfur compounds such as mercaptans, sulfides, and disulfides. Sulfide corrosion products can also act as depolarizers (Behret et al., 1975). Geesey et al. (1986) have recently demonstrated that the extracellular polymers secreted by bacteria can play a role in the corrosion of copper alloys.

This paper will present case studies of microbiologically influenced corrosion in a copper seawater piping system after a service life of approximately one year and in nickel alloy tubing after exposure to estuarine water for six months. A discussion of possible microbiologically influenced corrosion mechanisms is included.

CASE HISTORIES

Copper Alloy

A heavily pitted section of copper/nickel piping (88.5% copper, 10% nickel and 1.5% iron) (15 cm I.D., wall thickness 3.6 mm) was removed from the seawater piping system of a surface ship after approximately one year of seawater service. During operation of the ship, the seawater piping system had been maintained with continuously flowing seawater (1.6 m sec^{-1}) at a maximum temperature of 30°C . During the twelve to eighteen months of the shipbuilding process, however, the system had been operated with estuarine water from the Gulf of Mexico with intermittent flow and long periods of stagnation.

Surface deposits were thick and multilayered (Figure 2), varying in color with depth. Outermost layers were dark green to reddish-brown. Bright bluish-green deposits were found on the surface in unpitted areas. Pit interiors were black. Pit depths were typically 1.7–2.0 mm. Surface chemical and microbiological characterizations were performed with a KEVEX-7000 energy-dispersive X-ray spectrometer (EDAX) coupled to an AMRAY 1000A scanning electron microscope. A cross-section through the pitted areas exposed subsurface bacteria within the thin black deposit (Figure 3) and a spongy subsurface. An EDAX spectrum (Figure 4a) of the base metal shows the relative concentrations of iron, nickel and copper. The layer containing the bacteria, examined at two locations, showed consistent accumulations of phosphorus, sulfur, calcium and chlorine (Figure 4b, c) in addition to elevated amounts of iron and nickel. The spongy layer under the bacteria included an accumulation of phosphorus and a depletion of nickel (Figure 4d). Numbers of sulfate-reducing bacteria in the flow-through water and in the biofilm were estimated by the Most Probable Number (MPN) method using a medium containing lactate as the electron donor and carbon source made to the salinity of the seawater (Pfennig et al., 1981). Scrapings from the area within the pits indicated the presence of 1×10^5 sulfate-reducing bacteria cm^{-2} . Within the surface film on the unpitted surface, 1×10^1 sulfate-reducing bacteria cm^{-2} were detected.

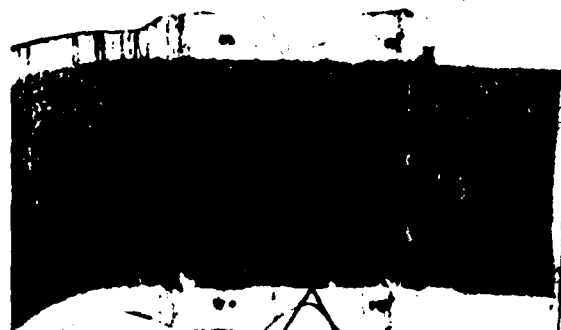
Water removed from the failed pipe section was typical of seawater: salinity, 35 parts per thousand; dissolved oxygen, 6.4 mg l^{-1} ; pH, 8.2; total organic carbon, 1.8 mg l^{-1} ; total suspended solids, 3.0 mg l^{-1} ; and total dissolved sulfate, 2.4 g l^{-1} . Dissolved sulfides were below the detection limits. The sulfate-reducing bacterial population in the seawater was typically $1 \times 10^1 - 10^2 \text{ cc}^{-1}$.

Nickel Alloy

Visual examination of the nickel alloy (66.5% nickel, 31.5% copper and 1.25% iron) after exposure to estuarine Gulf of Mexico water for six months indicated a multilayered scale with localized pitting (Figure 5). The average pit depth was 1.0 mm. Surface scales were characterized by blisters (Figure 6a, c) containing corrosion products and concentrations of bacteria. Numbers of sulfate-reducing bacteria within the surface deposits were typically $1 \times 10^4 \text{ cm}^{-2}$. Removal of the scale exposed localized, irregular-shaped pits (0.3–0.5 mm wide $\times$ 0.8–1.2 mm deep) (Figures 6b, d). The unexposed nickel alloy contained copper, nickel, manganese, and iron (Figure 7a). The EDAX spectrum from the black layer within the pits showed accumulations of sulfur and chlorine and increased amounts of iron compared to the base alloy (Figure 7b). Physical removal of the biofilm from the pit exposed a region depleted in nickel and iron (Figure 7c) containing an increased proportion of copper.

Gulf of Mexico estuarine water temperature varied from 9°C to 30°C ; pH varied from 7.4 to 8.2; chlorinity,

(a)



(b)

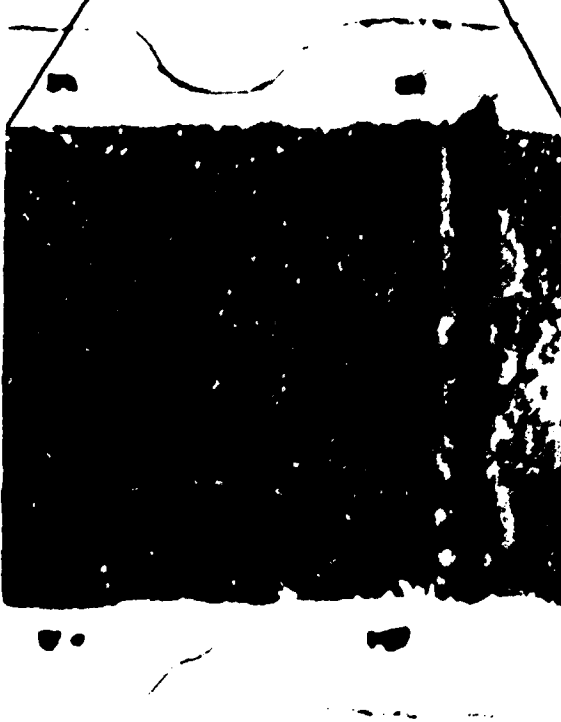


Figure 2. Cross-section of 2.5 cm I.D. copper alloy piping after one year in seawater service, showing thick surface deposits and pitting.

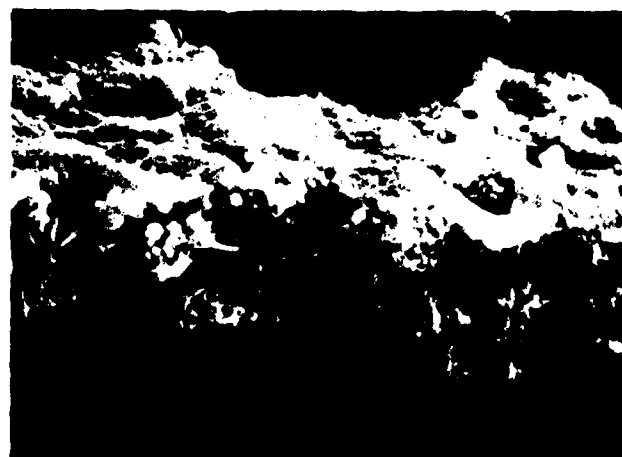


Figure 3. Scanning electron micrograph of a cross-section of the black deposit within a pit of copper alloy. Bacteria are within black deposit. A spongy copper-rich region is beneath the bacteria.

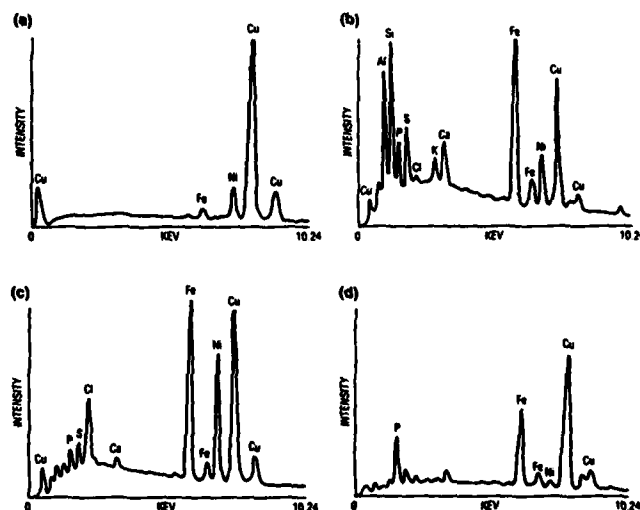


Figure 4. (a) EDAX spectrum of clean copper alloy before exposure (b) EDAX spectrum of pitted region of copper alloy, showing accumulation of aluminum, silicon, phosphorus, sulfur, calcium and elevated amounts of iron and nickel. (c) EDAX spectrum of pitted region of copper alloy, showing the accumulation of chlorine and elevated amounts of iron and nickel. (d) EDAX spectrum of spongy material beneath bacteria, showing an accumulation of phosphorus, an enrichment of iron and a depletion of nickel in the base of the pit.



Figure 5. Cross-section of 20 mm I.D. nickel tube after exposure to estuarine water for six months showing surface deposits and pitting.

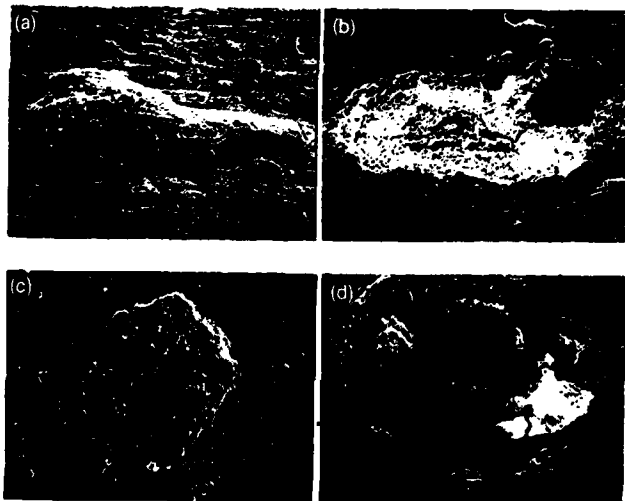


Figure 6. (a) and (c) Blisters on the surface of nickel tube. (b) and (d) Pits in nickel tube.

from 4.3 to 20.0 parts per thousand Cl^- , indicating a range of salinity from 7.7 to 36 parts per thousand. Total suspended solids ranged from 10 to 65 mg l^{-1} . Dissolved oxygen varied from 4.3 mg l^{-1} during the summer to 10.8 mg l^{-1} during the winter months. Dissolved sulfides were below detection limits. The mean concentration for sulfates (SO_4^{2-}) was 2.5 gram l^{-1} . The MPN for sulfate-reducing bacteria in the estuarine water was 1×10^2 to 10^3 cc^{-1} .

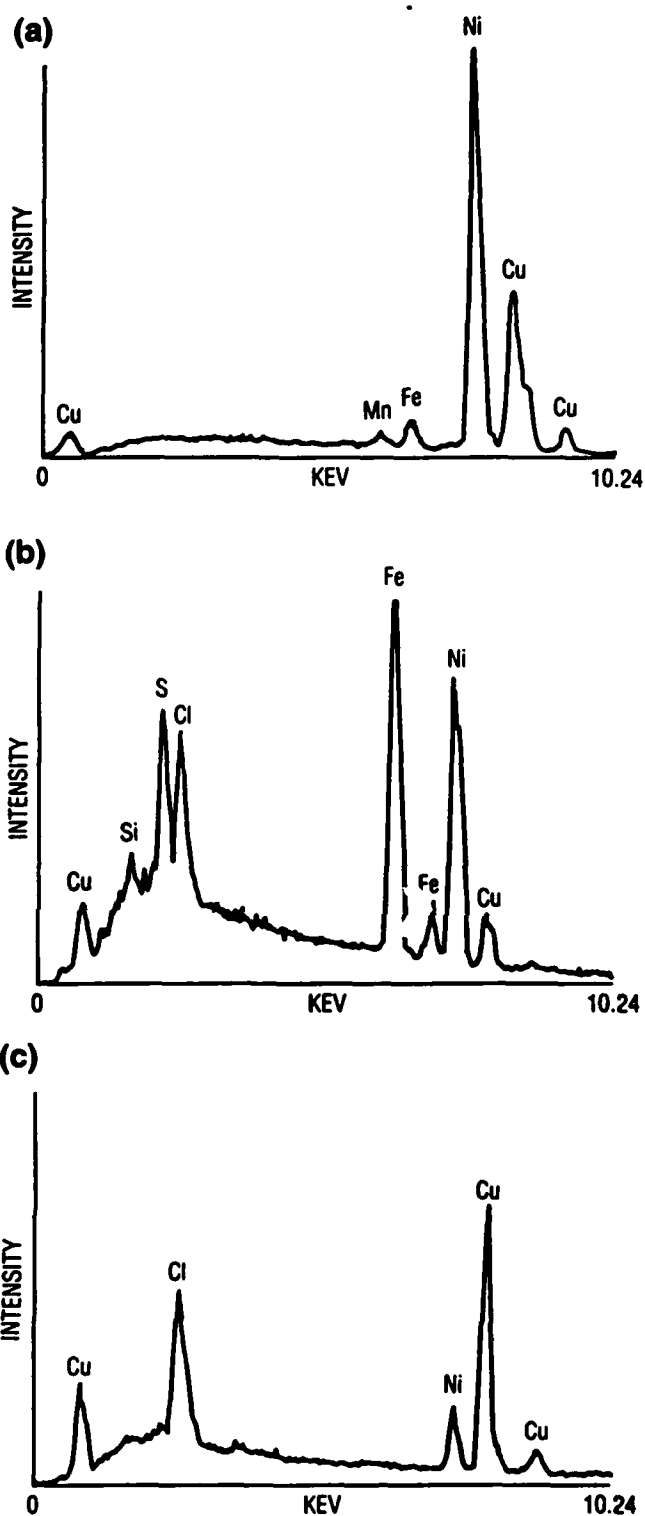


Figure 7. (a) EDAX spectrum of unexposed nickel alloy. (b) EDAX spectrum of nickel alloy after exposure to estuarine water for six months showing accumulations of silicon, sulfur, and chlorine with elevated concentrations of iron and nickel. (c) EDAX spectrum of the residual metal in the base of the pit showing nickel depletion and copper enrichment.

DISCUSSION

Copper alloys prevent or retard the settlement of macrofouling species, such as barnacles and mussels (Moreton and Glover, 1980; Fischer et al., 1981; Roberts, 1976). However, bacteria, microalgae, protozoa, and their cellular exudates form a slime layer on copper-containing surfaces (Danile and Chamberlain, 1981; Field, 1981; Purkiss, 1970). Marszalek et al. (1979) documented that copper fouled at a slower rate than stainless steel and glass surfaces and that the microflora on copper surfaces was less diverse than that found on the steel and glass exposed under identical conditions to Gulf Stream water in Key Biscayne, Florida. They reported that fungi were conspicuously absent on the copper surfaces and diatoms appeared only after copper surfaces were covered with a microfouling layer populated with bacteria and copious amounts of extracellular polymer. It has been reported that both macrofouling and microfouling increase as the concentration of nickel in the alloy increases (Uhlig and Revie, 1985).

Corrosion can range from highly uniform to highly localized. In uniform corrosion the anodic and cathodic sites are difficult to discriminate experimentally, while in localized corrosion they are not. Crevice corrosion, filiform corrosion, pitting, selective leaching and erosion-corrosion are typical forms of localized corrosion. No general theories apply to all forms of localized corrosion. Nevertheless, the following factors are frequently important: cathode:anode surface area ratio, differential aeration, and pH changes at anodic and cathodic sites. Most confirmed cases of microbiologically influenced corrosion are characterized as localized corrosion (Characklis et al., 1989; Videla, 1985; Tatnall, 1981; Kobrin, 1976). Discrete mounds or columns develop on metal surfaces as a result of microbial activities and result in a localization of anodic and cathodic reactions.

Pitting in predominantly copper alloys has been attributed to under-deposit attack (Figure 8a). Under-deposit corrosion is extremely important for these alloys because it initiates a series of events that are individually or collectively extremely corrosive (Shreir, 1977). Dead barnacles, dirt, debris or microbiological colonies accumulating on the surface result in the formation of differential aeration cells (Figure 8b). In an oxygenated environment, such as unpolluted natural seawater, the area immediately under the deposit becomes deprived of oxygen. That area becomes a relatively small anode compared to the large surrounding oxygenated cathode. Cathodic reduction of oxygen may result in an increase in pH of the solution in the vicinity of the metal. At the anodic site the metal will form metal cations. If the metal hydroxide is the thermodynamically stable phase in the solution, the metal ions will be hydrolyzed by water with the formation of H^+ ions. If the cathodic and anodic sites are separated from one another, the pH at the anode will decrease and that at the cathode will increase. Cl^- from the electrolyte will migrate to the anode to neutralize any buildup of charge (Hoar, 1947). The low solubility of copper chlorides and hydroxychlorides maintains

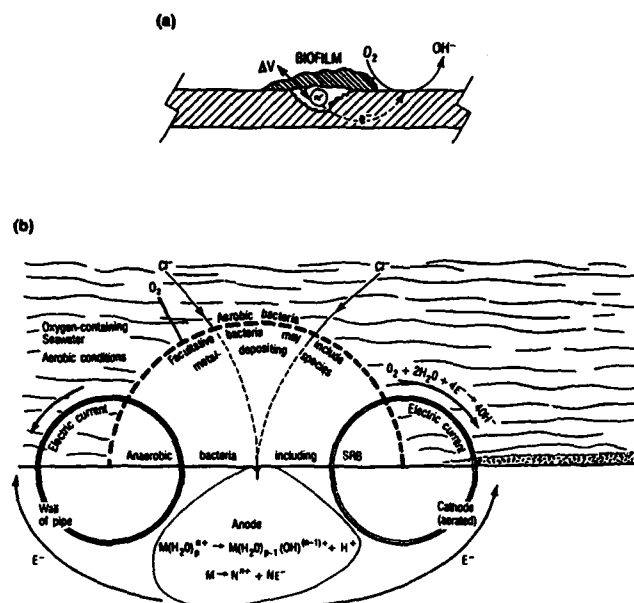


Figure 8. (a) Differential aeration cell formed by microbial colonies. (b) Detailed reactions resulting from the formation of a differential aeration cell.

the activity of copper ions at a low value and facilitates anodic dissolution of the copper. Under these circumstances, pitting in copper alloys involves the conventional features of differential aeration, a large cathode:anode surface area ratio, and the development of acidity within the pit. Under some conditions this can lead to the formation of nantokite, $CuCl$, and a form of corrosion termed "bronze disease" (Scott, 1990).

Geesey et al. (1986) have demonstrated that the exopolymers that anchor cells to surfaces exhibit saturation binding of copper ions in aqueous suspensions. Microcolonies within a biofilm have the capacity to form copper concentration cells with adjacent areas in a biofilm that contain less reactive polymer, promoting deterioration of copper surfaces. The concentration cells are maintained by the acid-producing activities of the biofilm microflora.

In the two case studies reported, sulfate-reducing bacteria were isolated from localized deposits associated with the pits. Sulfate-reducing bacteria are a diverse group of anaerobic bacteria that can be isolated from a variety of environments (Pfennig et al., 1981; Postgate, 1979), including seawater (Battersby, 1988), where the concentration of sulfate is typically 2 grams per liter. Even though the oxygen content of seawater ranges from 6–10 ppm, anaerobic microorganisms can survive in anaerobic microniches until conditions are suitable for their growth (Costerton and Geesey, 1986; Staffeldt and Kohler, 1973). Seawater piping systems have high surface areas at which nutrients can concentrate, predisposing these systems to biofilm formation (Costerton et al.,

1987). If the aerobic respiration rate within the biofilm is greater than the oxygen diffusion rate, the metal/biofilm interface can become anaerobic and provide a niche for sulfide production by sulfate-reducing bacteria (Little et al., 1990).

The impact of sulfides on the corrosion of copper alloys has received a considerable amount of attention. Little et al. (1988, 1989) have published several reports documenting localized corrosion of copper alloys by sulfate-reducing bacteria in estuarine environments. Others have reported the failure of copper alloys in polluted seawater containing waterborne sulfides that stimulate pitting and stress corrosion cracking (Rowlands, 1965). Copper alloys suffer accelerated corrosion attack in seawater containing 0.01 ppm sulfide after one-day exposure (Gudas and Hack, 1979). A porous layer of cuprous sulfide with the general stoichiometry $\text{Cu}_2 - x\text{S}$, $0 < x < 1$ forms in the presence of sulfide ions (Syrett, 1980). Copper ions migrate through the layer, react with more sulfide, and produce a thick, black scale (Figure 9a). Under these conditions, corrosion is under cathodic control, limited by the diffusion of H^+ ions to the cathodic sites (Syrett, 1980; Macdonald et al., 1979). The role of cathodic depolarization is not adequately understood and may be a transient phenomenon.

It has been argued that if the copper sulfide layer were djurelite ($\text{Cu}_{1.96}\text{S}$) the sulfide layer would be protective (North and MacLeod, 1986). Even if such a sulfide film were technically passivating (Figure 9a), the film's mechanical stability is so poor that sulfide films are useless for corrosion protection. In the presence of turbulence, the loosely adherent sulfide film is removed, exposing a fresh copper surface to react with the sulfide

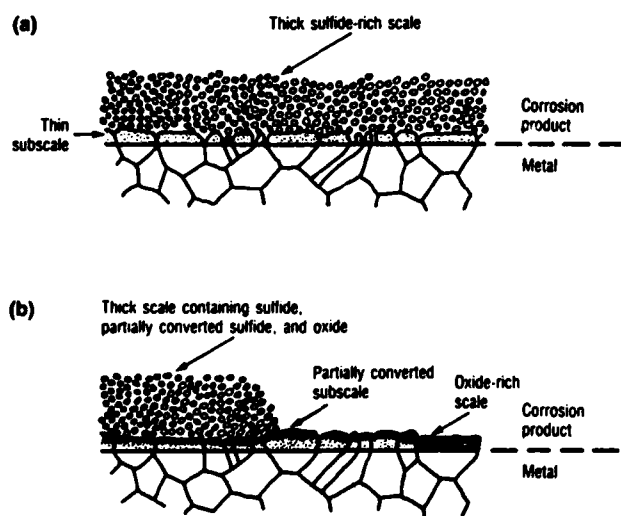


Figure 9. (a) Schematic of thick sulfide-rich scale forming on copper alloy (Taken from Syrett, 1980 with permission). (b) Schematic showing disruption of sulfide-rich film on copper alloy by the introduction of aerated seawater (Taken from Syrett, 1980 with permission).

ions. For these reasons turbulence-induced corrosion and sulfide attack of copper alloys cannot be decoupled easily. In the presence of oxygen, the possible corrosion reactions in a copper sulfide system are extremely complex because of the large number of stable copper sulfides (Ribbe, 1976), their differing electrical conductivities, and catalytic effects. Transformations between sulfides, or of sulfides to oxides, result in changes in volume that weaken the attachment scale and oxide subscale leading to spalling. Bared areas repassivate, thus forming cuprous oxide (Figure 9b).

Pope (1986) has isolated sulfate-reducing bacteria from 90/10 copper/nickel surfaces under deposits of iron- and manganese-oxidizing bacteria and under discrete deposits of slime-forming organisms where severe pitting was observed. The pits under the deposits contained up to several million sulfate-reducing bacteria per pit. It was proposed that the deposits were formed by the action of slime-forming organisms and iron- and manganese-depositing bacteria that precipitate metals in the hydroxide forms. These surface deposits provide an anaerobic environment that permits the growth of sulfate-reducing bacteria and the production of corrosive metabolic products.

EDAX spectra for the pitted copper alloy indicate that nickel had been selectively removed from the alloy in the presence of sulfate-reducing bacteria. Verink and Pourbaix (1971) and Efird (1970) reported denickelification of Cu/Ni alloys associated with occluded cells in salt solutions where lowering of the pH had taken place. A detailed discussion of the mechanisms for selective attack and dealloying has been addressed by Shreir (1977b).

Nickel is generally regarded as a corrosion-resistant material. In flowing seawater the reported corrosion rate is typically 0.012 mm/yr. Alloys containing more than 40 percent Ni tend to show the passivity associated with pure Ni. The passive layer that forms on nickel alloys is not impaired under turbulent conditions (May and Welden, 1965). However, high nickel alloys do exhibit a tendency toward pitting corrosion.

Because the pitting potential of nickel/copper alloy is typically within 20–30 mV of the open circuit potential (Bates and Popplewell, 1975), these alloys have a marked tendency for the initiation of pitting in chloride-containing environments where the passive film can be disturbed. Under stagnant conditions, chlorides can penetrate the passive film at weak points and cause pitting attack. Sulfides can cause either a modification of the oxide layer as described for copper or breakdown of the oxide film of nickel based alloys. Pit initiation and propagation depend on the depth of exposure, temperature, and presence of surface deposits (Maylor, 1978; Southwell and Alexander, 1967; Gouda et al., 1990).

Schumacher (1979) reported that predominantly nickel alloys were susceptible to under-deposit corrosion and oxygen concentration cells (Figure 8 a,b). Gouda et al. (1990) demonstrated pitting of nickel/copper tubes

exposed in Arabian Gulf seawater. In their studies, pits developed under deposits of sulfate-reducing bacteria and nickel had been selectively dealloyed.

The microbiologically influenced corrosion of nickel reported in this paper was characterized by the formation of blisters and pits containing sulfate-reducing bacteria. Differential aeration cells appear to have been formed, with low oxygen concentration immediately underneath the deposits. This created an environment for the growth and activities of sulfate-reducing bacteria. The surface area under the deposit became anodic and corroded while the electrons that were generated reacted at the cathodic region of high oxygen concentration. Chlorine and sulfur accumulated within the region of the pit and reacted with the iron and nickel in the alloy. Nickel had been selectively removed from the alloy, leaving a spongy copper-rich material in the base of the pit.

CONCLUSIONS

Copper and nickel alloys used in seawater environments can suffer from microbiologically influenced corrosion. In the two case studies reported, pitting occurred under surface deposits containing 10^4 – 10^5 sulfate-reducing bacteria cm^{-2} . Possible mechanisms for the observed pitting include the formation of differential aeration cells that increase the cathode:anode area ratio, initiating the formation of an acidic environment within the pit. Chlorine and sulfur accumulated in the pits of both alloys, and nickel was selectively removed from the pitted regions.

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