

AN INVESTIGATION OF MICROBIOLOGICALLY MEDIATED CORROSION OF COPPER-NICKEL  
PIPING SYSTEMS SELECTIVELY TREATED WITH FERROUS SULFATE

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ABSTRACT

Microbiologically induced corrosion in 90/10 Cu-Ni pipes was evaluated using estuarine water from the Gulf of Mexico at the mouth of the Pascagoula River, maintained at a flow rate of 3-6 ft/sec over an 8-month period. The impact of surface preparation, batch  $\text{FeSO}_4$  (50 ppb  $\text{Fe}^{2+}$  for 48 hours) pretreatment and intermittent treatment was evaluated. Surface deposits were characterized by scanning electron microscopy and energy-dispersive x-ray fluorescence spectrometry. Water analyses included pH, dissolved oxygen, dissolved sulfide and sulfate, total organic carbon, total suspended solids and dissolved heavy metal analyses, as well as quantification of bacteriological components.

Batch  $\text{FeSO}_4$  treatment did not result in a persistent increase in surface-bound iron or decreased localized corrosion. Surface pitting appeared to be associated with accumulations of chlorine, sulfur, and microbiological colonization.

1. INTRODUCTION

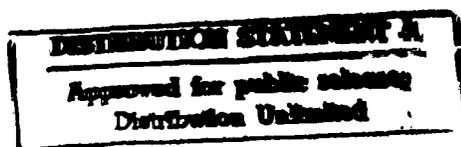
Copper alloys have a long history of successful application in seawater piping systems due to their corrosion resistance, antifouling properties, and mechanical properties. The corrosion resistance of copper in seawater is attributable to the formation of a protective film that is predominantly cuprous oxide, irrespective of alloy composition [1]. Often, basic chloride atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) or malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), a carbonate salt, form a bulky, green, nonprotective film that overlies the  $\text{Cu}_2\text{O}$  layer [2].

Copper alloys are susceptible to some types of corrosion and premature corrosion failures have been reported [3,4]. Failure of copper-nickel pipes in polluted estuarine water can be associated with waterborne sulfides that stimulate pitting and stress corrosion cracking [5]. 90/10 copper nickel was shown to suffer accelerated corrosion attack in seawater containing 0.01 ppm sulfide after a 1-day exposure [6]. There can also be changes in the galvanic relationships between normally compatible piping and fitting alloys in sulfide containing seawater [7]. Copper alloys are vulnerable to erosion corrosion caused by the removal or breakdown of the protective film by mechanical forces such as local turbulence and impingement [8].

Copper alloys are also susceptible to microbiologically induced corrosion (MIC). Pope [9] proposed the following mechanisms for microbial attack: production of corrosive substances, e.g.,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , organic or inorganic acids; production of metabolites that act as depolarizers; and anaerobically produced mercaptans and disulfides through the microbial transformation of sulfur compounds.

As the  $\text{Cu}_2\text{O}$  corrosion film forms in seawater, copper ions and electrons must pass through the film to support anodic and cathodic half-reactions. It has been shown experimentally that alloying additions of nickel and iron into the highly defective p-type  $\text{Cu}_2\text{O}$  corrosion product film as dopants alters the structure [1] and results in a corrosion film that possesses low electronic and ionic conductivity [10]. Such a film has been shown to be resistant to waterborne sulfides and impingement attack [8]. CDA 706, an alloy containing 88.5% copper, 10% nickel, and 1.5% iron, has been shown to be the most corrosion-resistant copper-based alloy [11]. Both alloyed and precipitated iron are effective methods for introducing iron into the  $\text{Cu}_2\text{O}$  [9]. Ferrous ions may be added to seawater in a variety of ways, including periodic batch additions of ferrous sulfate crystals, continuous injection of ferrous sulfate solutions, or the use of naturally occurring iron corrosion products [12-19]. In the presence of naturally occurring anodes and cathodes,  $\text{Fe}^{2+}$  ions form lepidocrocite  $7\text{-FeOOH}$ , a colloidal hydrous oxide capable of interacting with cations at pH values 6-8. It has been shown that the positively charged colloid can migrate and adhere to a negatively charged cathode. It subsequently spreads over the entire surface to form a nonconducting film that impedes electron transfer between the copper and dissolved electron acceptors. Since the corrosion of the copper-nickel alloys in aerated, unpolluted seawater is cathodically controlled by oxygen reduction (oxygen is the electron acceptor), the  $\text{FeOOH}$  is a cathodic inhibitor; furthermore, Hack [20] reported that continuous  $\text{FeSO}_4$  injections prevented sulfide-induced corrosion of copper-nickel alloys by stripping corrosive sulfides from solution before reaction with the pipe surface was possible. The efficacy of  $\text{FeSO}_4$  treatments has never been evaluated as a means of controlling MIC.

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Both  $\text{FeSO}_4$ -treated and untreated CDA 706 seawater piping systems on U. S. Navy ships have experienced premature corrosion failures. Most of the failures have been attributed to turbulence and impingement attack. However, some failed sections are characterized by a nonhomogeneous, nonadherent surface film with subsurface pitting. The surface films contained calcium, sulfur, chlorine, silica and iron, in addition to copper and nickel, and accumulations of microorganisms [21].

In an attempt to understand the failure mechanism in such pipe sections and the role of  $\text{FeSO}_4$ , a dockside experiment was undertaken at a ship construction site at Ingalls Shipbuilding Division, Litcon Industries, Pascagoula, Mississippi. The flow-through water was the naturally occurring estuarine water from the mouth of the Pascagoula River in the Gulf of Mexico. Batch ferrous sulfate surface treatment of CDA 706 copper-nickel piping systems was evaluated in the presence of biofilms containing sulfate-reducing bacteria. The corrosion of  $\text{FeSO}_4$ -treated pipes was compared to untreated pipes that had been cleaned according to military specifications.

## 2. METHODS AND MATERIALS

Eight-foot sections of CDA 706 Cu-Ni pipes were pretreated and maintained as indicated in Table 1. Pipes treated with ferrous sulfate were exposed to a 50 ppb solution of  $\text{Fe}^{+2}$  for 48 hours. The solution was prepared as follows: a 20% (by weight) stock solution (pH 1.7, stabilized with sulfuric acid) of ferrous sulfate prepared the day it was to be used and diluted to 50 ppb, pH 7.7, prior to treatment.

The cleaning of Case 4 consisted of a soak with a general purpose detergent [22] mixed with hot tap water, a flush with tap water, and air drying. The extensive cleaning in Case 5 consisted of a soak in a mixture of tri-sodium phosphate ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ), [23] general purpose detergent [22] and hot tap water. This mixture was introduced into the piping system for 12 hours. The system was flushed with hot tap water. The pipe was then exposed to a mixture of citric acid [24] for a period of 6 hours, drained, flushed with tap water, and air dried.

Table 1. Pipe Treatments and History

- Case 1: Installed without pretreatment, allowed to biofoul (2 months)(2 weeks), stagnated and then exposed to continuous flow conditions.
- Case 2: Installed without pretreatment, allowed to biofoul (5 months), then treated with  $\text{FeSO}_4$ .
- Case 3: Pretreated with  $\text{FeSO}_4$ .
- Case 4: Pretreated with normal shipyard cleaning (soak, flush, hydro, cleaning).
- Case 5: Fabricated with bends, braze joints, socket and butt welding (exaggerated cleaning).

Pipes were maintained on the Westbank Dock at Ingalls. The intake water was from a 22 ft depth and maintained at a flow rate of  $3\text{-}6 \text{ ft sec}^{-1}$ , as indicated in Figure 1. Sections from pipes 1-4 were removed biweekly, preserved in 4% buffered glutaraldehyde, and subsectioned in the laboratory. Surface chemical analyses were performed with a KEVEX-7000 energy-dispersive x-ray spectrometer (EDAX) coupled to an AMRay 1000A Scanning Electron Microscope (SEM). Subsections were sputter-coated with gold before photography with the SEM. Case 5 will be sectioned at the conclusion of the experiment.

Water samples for chemical analyses were collected at the intake depth. PH [25], chlorinity [25], dissolved oxygen [26], suspended solids [25], temperature [25], total iron [25], and total copper [25] concentrations were monitored weekly by Ingalls. Dissolved sulfides were measured biweekly using a modification of a method described by Strickland and Parsons [27]. The modification uses a 10-cm cell to increase sensitivity. The detection limit of the modified method is 6.5 ppb. Total sulfate concentration [25] was measured bimonthly. Total organic carbon [25] and ferrous iron [25] concentrations were measured intermittently. Microbiological analyses were performed periodically to determine the concentration of sulfate-reducing bacteria in the flow-through water using the American Petroleum Institute technique [28] which involves serial dilution in anaerobic bottles containing a nail as a source of iron.

## 3. RESULTS

Water temperature varied from  $9^\circ$  to  $17^\circ\text{C}$  over the experimental period extending from September 1986 to February 1987. The pH varied from 7.4 to 8.2.

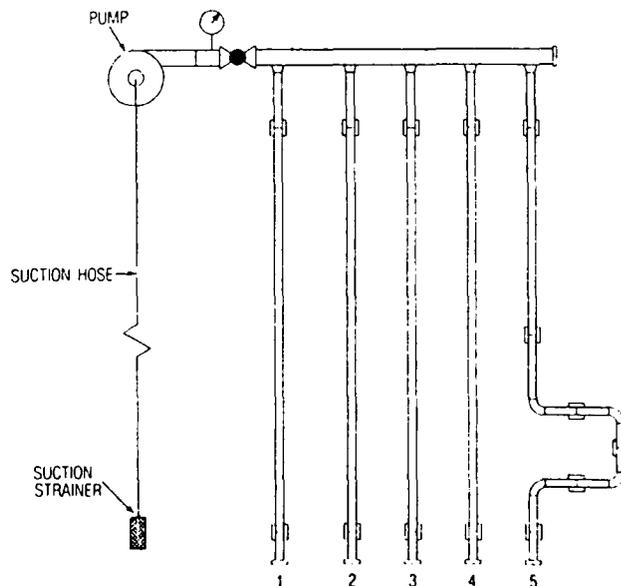


Figure 1. Flow diagram of dockside experiment

Chlorinity varied from 4.3 to 20.0 ppt  $\text{Cl}^-$ . Chlorinity can be converted to salinity using the following relationship: Salinity (ppt) = 1.806 Chlorinity (ppt). Total suspended solids ranged from 10 ppm to 65 ppm during dredging operations. Dissolved oxygen varied from 5.2 ppm during September to 10.5 ppm in late December. Copper and iron concentrations in the river water fluctuated between 5 to 70 ppb and 150 to 906 ppb, respectively. Dissolved sulfides could not be detected during the experiment. The mean concentration for sulfates ( $\text{SO}_4^{2-}$ ) was  $\approx 2500$  mg/l. Standard plate counts indicated bacterial populations of  $1 \times 10^4$  -  $10^5$  per cc and a sulfate-reducing bacterial population of  $1 \times 10^2$  -  $10^3$  per cc.

The EDAX spectra of the pipe surfaces were essentially identical despite the varying initial treatments. Pipe surfaces were predominantly copper, nickel, and iron. A sample spectrum is shown in Figure 2. Over the 8-month exposure period, all surfaces exposed to Pascagoula River water accumulated silica, phosphorus, sulfur, chlorine, potassium, and calcium (Fig. 3). Pipes 2 and 3 did show a temporary increase in surface Fe immediately after batch treatment. However, this increase was not evident at the next sample collection after two weeks.

The appearance of the pipe interiors was markedly different after 2 months. Despite the stagnation in pipe 1, pipes 1 and 4 had a tenacious reddish-brown film on the surface. There was no surface pitting on these two surfaces. Pipes 2 and 3 were covered with a patchy, flaky, green film characterized by blisters that have persisted over the 8-month evaluation period. Figure 4 shows the pipe interiors after 6 months of exposure. Well-defined biofilms developed on all surfaces (Figs. 5-6). Within the blisters found on pipes 2 and 3, bacterial cells were observed (Figs. 7-9). Surface pitting was found beneath the blisters (Fig. 10).

#### 4. DISCUSSION

In the dockside experiment reported here, the impact of batch  $\text{FeSO}_4$  treatment in the presence of microorganisms was evaluated over an 8-month period. The straight lengths of pipe maintained at flow rates of 3-6 ft second<sup>-1</sup> were designed to eliminate the possibility of impingement attack and to maximize the possibility for microbial colonization.

The mechanism of accelerated corrosion of copper-nickel alloys in sulfide-polluted seawater has been summarized by Syrett [4]. During the first few seconds of exposure to sulfide-polluted water, a thin film forms on the copper surface that is primarily cuprous oxide. Cuprous sulfide forms soon after the alloy is exposed to the polluted seawater. The chemical composition of the oxide-type film is variable, but its sulfur content never approaches that of the cuprous sulfide scale that grows on top of it. The initial anodic reaction product is  $\text{Cu}^+$  ions that react with the dissolved sulfide and precipitate at the metal surface to produce a porous black scale. The cathodic

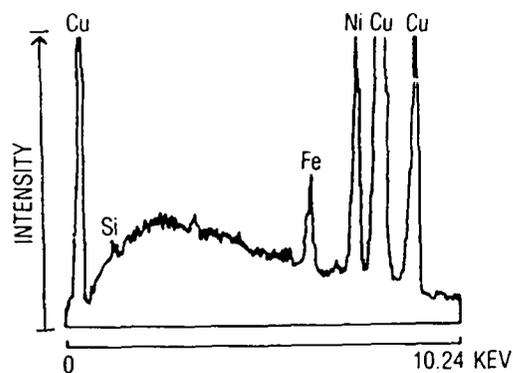


Figure 2. Representative EDAX spectrum of pipe surfaces after initial treatments

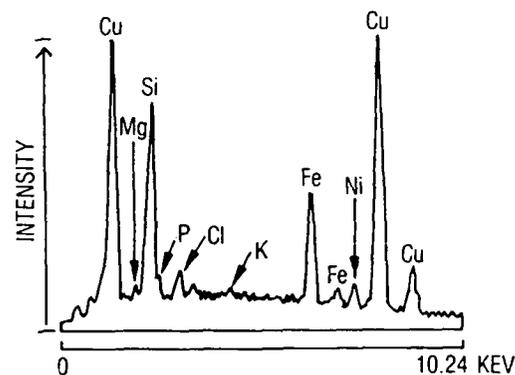


Figure 3. Representative EDAX spectrum of pipe surfaces after 6 month exposure period

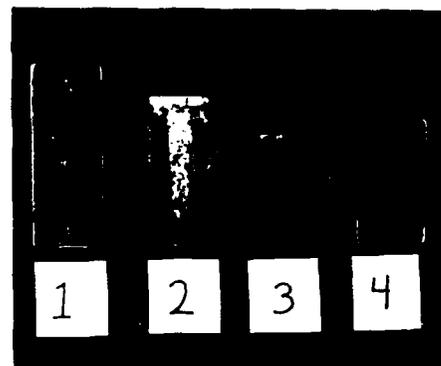


Figure 4. Pipe interiors after 6 months exposure

reaction,  $\text{H}^+$  ion reduction, occurs at the boundary between the oxide-type and sulfide layers, and produces  $\text{OH}^-$  ions that can react with the anodically produced  $\text{Cu}^+$  ions. However, most of the  $\text{Cu}^+$  ions migrate through the porous  $\text{Cu}_2\text{S}$  scale, react with dissolved sulfide, and lead to a thickening of the scale. Under these conditions,

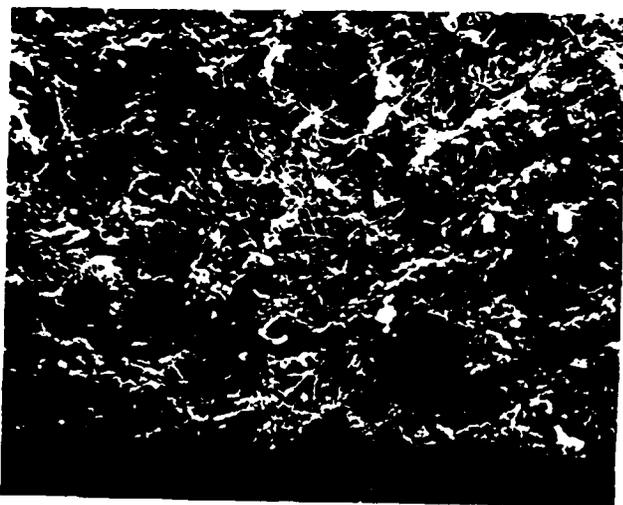


Figure 5. Biofilm on exposed surface of pipe 1

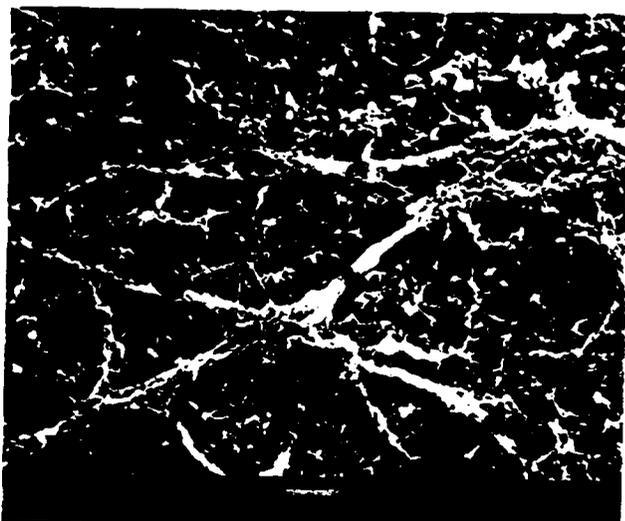


Figure 6. Biofilm on exposed surface of pipe 4

corrosion is under cathodic control, limited by the transport of  $H^+$  ions to the cathodic sites.

When sulfide-polluted, deaerated seawater is replaced by unpolluted, aerated seawater, the cathodic reaction rate increases, and the corrosion rate increases sharply.  $Cu^+$  ions diffusing through the porous sulfide scale combine with dissolved oxygen to produce  $Cu_2O$ , and the sulfide scale itself is slowly transformed to the oxide with the concomitant production of  $SO_4^{2-}$  ions or elemental sulfur. A reduction in the sulfur content of the oxide-type scale will also occur at a relatively low rate. The transformation of sulfide to oxide results in a change in volume that weakens the bond between the thick black scale and the oxide-type subscale and leads to spalling. Barred areas repassivate, forming cuprous oxide.



Figure 7. Blisters characterising the flaky film on pipe 2

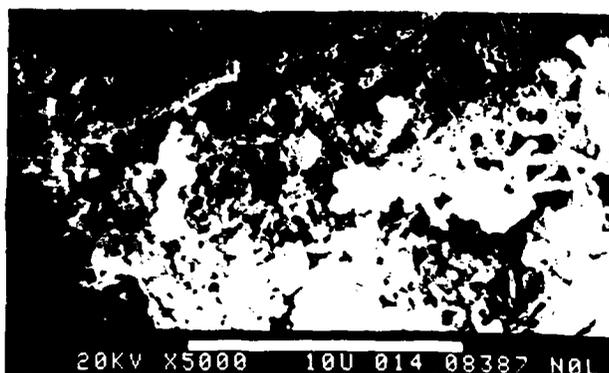


Figure 8. Bacterial cells observed within blister on pipe 3



Figure 9. Bacterial cells observed within blister on pipe 2



Figure 10. Surface pitting beneath blister on pipe 2

Waterborne sulfides could not be measured in the Pascagoula River water during the course of this experiment. Sulfide-induced corrosion in piping systems is often discounted because waterborne sulfides are below detection limits. Obligate anaerobic sulfate-reducing bacteria can exist in oxygenated waters, colonize a surface in anaerobic niches, and produce sulfides. Large concentrations of sulfates and sulfate-reducing bacteria were demonstrated in the Pascagoula River water. Furthermore, sulfur and chlorine accumulated on all pipe surfaces. The concentration of  $\text{Cl}^-$  on pipes 2 and 3 was enhanced relative to pipes 1 and 4. The formation of flaky nonadherent films only on pipes 2 and 3 and the presence of bacteria with blisters on those surfaces cannot be explained by the authors at this time.

Localized pitting of copper alloys under microbiological colonies or tubercles has been cited [29,30]. Others [31] have reported the corrosion of copper in the presence of sulfate-reducing bacteria. Sulfate-reducing bacteria have been shown to be responsible for the corrosion of copper alloys in underground pipe installations through the production of  $\text{H}_2\text{S}$ , which forms a sulfide film on the surface of the metal. Such a film is protective as long as it is continuous. Breaks in the film, however, expose areas where pitting can occur. Breaks in the wet surface films on pipes 2 and 3 were evident after 2 months exposure. Surface pitting was observed under blisters on these surfaces.

Total iron concentration in the flow-through water varied from 150 to 900 ppb. Of this amount, 65 ppb was shown to be  $\text{Fe}^{2+}$ . In the organic-rich water, a majority of the total iron concentration would be expected to be colloidal  $\gamma\text{-FeOOH}$  [32]. Since "Oxidants are consumed in order of decreasing energy production per mole of organic carbon oxidized ( $\text{O}_2$  > manganese oxides - nitrates > iron

oxides > sulfate)" [33] ferrous iron would be produced in the flow-through water before sulfides. Furthermore, the iron in the flow-through water is present in concentrations an order of magnitude greater than that introduced by batch treatment. Under such circumstances it is unlikely that water borne sulfides could cause corrosion.

## 5. CONCLUSIONS

The localized corrosion observed in the pipes of the dockside experiment appears to be due to microbiologically induced corrosion. Sulfate-reducing bacteria and sulfates were demonstrated in the flow-through water and sulfur accumulated in all surface deposits, which could result in an active/passive surface. Batch  $\text{FeSO}_4$  treatments did not result in a persistent increase in surface-bound iron. The persistent concentration of iron in the surface films was the same regardless of surface treatment, indicating that the iron in the surface film comes from the alloy, or the flow-through water, not the  $\text{FeSO}_4$  treatment. These observations apply only to batch  $\text{FeSO}_4$  treatment and cannot be used to predict the efficiency of  $\text{FeSO}_4$  injections or other applications of  $\text{Fe}^{2+}$  to surfaces.

## 6. ACKNOWLEDGMENTS

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