Unusual types of pitting corrosion of copper tubes in potable water systems


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I. INTRODUCTION

Copper tube has long been the standard for many plumbing applications throughout the world. Of the total copper consumption in Europe and the U.S. in 1989, copper tube represents 11 and 14%, respectively. This translates to approximately 250,000 tons of copper tube in each of these regions annually. The longstanding success of copper as a conduit for a wide variety of water delivery systems has been attributed to numerous features including durability, corrosion resistance, and antimicrobial activity.

Unusual pitting corrosion failures have, however, occurred in a small number of institutional buildings in different regions of the world in recent years. Incidences of an abnormal form of pitting corrosion were primarily in hot and cold water distribution systems of hospitals. While water provided from the mains to the facilities was initially potable, subsequent storage at some of the facilities may have resulted in changes in water quality before introduction to the water distribution system within the buildings. The pitting appeared to be unlike any previously reported failures. After extensive analysis, it was discovered that a film
of microbial origin was always present in areas where pitting was observed. The occurrence of a biofilm was believed to contribute in some way to this new form of pitting corrosion of copper plumbing material used in these institutional buildings.

Most corrosion engineers and scientists are not familiar with the potential roles that microbes may have in corrosion reactions. What are the criteria that can be used to implicate microorganisms in pitting corrosion of copper or other metals? It is usually the slimy texture of the corrosion deposit that leads most investigators to suggest a microbiological role. The slimy deposit is actually the result of the biofilm mode of growth. Ironically, biofilms are ubiquitous in nature and are present to varying degrees on virtually every surface in contact with nonsterile water. Microbial biofilms are present on corroding and noncorroding surfaces.

The reason that biofilms had not been associated with pitting corrosion of copper plumbing tube prior to 1985, when it was first reported in a German hospital, may be that no one specifically looked for or suspected their involvement. Although sulfate-reducing bacteria (SRB) had been implicated in certain types of corrosion as far back as the 1930s where anaerobic conditions and high sulfate concentrations occurred, microbiologically influenced corrosion (MIC) had not been considered to be important in the corrosion of copper tubing through which oxygen-containing water with low sulfate concentrations was circulated. Although polysaccharide-containing biofilms are present on most pipe surfaces, the detection of this and other microbial products led Fischer et al. to establish a connection between the microbiological slime layer and underlying pits in the corroding copper tubing in the hospitals where the problems have occurred. Considerable research has been conducted in the past 5 years to gain a better understanding of the role that biofilm microorganisms can play in pitting corrosion of copper tube. Through this research, we have obtained some understanding of the factors such as water chemistry, temperature and system design, installation, operation, and maintenance that predispose a system to corrosive microbial attack. This chapter summarizes what we have learned on this subject.

II. TYPES OF PITTING IN COPPER TUBE

A. Classical Types of Pitting

Several different types of pitting corrosion are known to occur in copper tubing used for water service in institutional buildings. Type 1 pitting occurs in cold water lines that contain water supplied from deep bore holes. This water contains low concentrations of microorganisms and organic carbon and high concentrations of dissolved inorganic ions. Pits develop in the inner wall of copper tube. The pits contain soft crystalline
cuprous oxide under a membrane of cuprous oxide crystals (Figure 1). Cuprous chloride also occurs in the pits. Basic copper carbonate mounds occur over the pits. Type 1 pitting occurs in the presence of certain hard well waters. Luce has shown that Type 1 pitting propensity of such waters depends on pH, dissolved oxygen, chloride, sulfate, sodium, and nitrate. There are no indications to date which suggest that microorganisms are involved in this type of pitting corrosion.

Copper tubing is fabricated to different hardness: hard, half-hard, and soft. In the past, a film derived from the drawing lubricant that becomes carbonized during the softening (bright annealing) process has been related in a rather complicated way to Type 1 pitting corrosion of annealed copper tube. Abrasive cleaning or controlled oxidation of the tube bore is now carried out as a final step in the manufacturing process to remove the film. Hard-drawn tubes, not being bright annealed in the course of fabrication, are much less likely to contain carbon films. However, carbon films are sometimes found in hard-drawn tubes, presumably as a result of exposure to unusually high temperatures during the drawing process. No influence of tube hardness has been detected with respect to the unusual type of pitting corrosion.

Type 2 pitting occurs in systems which circulate hot, soft water. The pits contain hard, crystalline cuprous oxide and are covered by small nodules composed of copper oxides and basic copper sulfate (Figure 1). An adherent cupric oxide-cuprous oxide layer exists over the unpitted surface. Type 2 pitting occurs primarily at temperatures above 60°C or where the water is below pH 7.4 or where the bicarbonate-sulfate ratio
in the water is less than 1. Like Type 1 pitting, no evidence currently exists that suggests microbiological involvement in this form of pitting corrosion.

Type 3 pitting is characterized by groups of small hemispherical pits under a common covering of basic copper sulfate. An oxide membrane extends across all the pits in the group with a perforation above the center of each pit. Up to 1% sulfide may be found in the pits. This type of pitting occurs in pipes carrying cold water with high pH, low hardness, and low mineral and low organic content. This type of pitting has been restricted to two areas in Sweden. No involvement of microorganisms has been demonstrated in this type of pitting corrosion.

B. Unusual Types of Pitting

Two unusual types of pitting corrosion have been observed which are thought to involve microbial biofilms. One resembles Type 3 in that numerous pits occur beneath a common basic copper sulfate crust with the oxide membrane across the pits being randomly perforated. This type of pitting has been reported in certain hospitals in southwest Scotland which use surface waters that contain relatively high concentrations of dissolved organic compounds, suspended particulates including microorganisms, and low buffering capacity (pH 7.4 to 9.3). The other new type of pitting occurs in cold, warm, and hot water systems and exhibits features of both Type 1 and Type 2 pitting (Figure 2). It resembles Type 1 pitting in that the pits are hemispherical and contain soft crystalline cuprous oxide with varying amounts of cuprous chloride under a
cuprous oxide membrane. It resembles Type 2 pitting in that the oxide on the surface between the pits is largely cupric. The mounds above the pits are principally basic copper sulfate, often with a deposit of powdery cupric oxide around the periphery and on parts of the deposit itself.

Immersion of the tubing in 25% nitric acid indicated the absence of a carbon film and hence the pitting was not Type 1. A dried gelatinous film was present that stained positive with periodic acid Schiffs base (PAS) reagent or Gentiana violet, indicating the presence of polysaccharide. This unusual type of pitting has been referred to as “Type 1 1/2” pitting and has been in Saudi Arabia, Germany, Scotland, and more recently in southwest England. A description of the corrosion products from copper tubing collected from the various institutional facilities has been reviewed.

With one exception, cases in which these unusual types of pitting occurred were from soft water supplies. The waters in which the unusual type of pitting corrosion have been observed have total hardness of between 25 to 40 mg/l CaCO₃, alkalinity (carbonate hardness) between 10 and 20 mg/l CaCO₃, chloride between 15 and 20 mg/l, and sulfate between 10 and 30 mg/l. In most cases, the sulfate content is approximately twice the carbonate content. Since the water is so poorly buffered, pH is quite variable in water associated with this type of pitting. A more complete description of water characteristics where the unusual types of pitting corrosion have been observed is presented by Fischer et al. and by Wagner et al.

In addition to those cases described above, there have been other reports of pitting corrosion in copper tube exposed to soft supply waters containing chloride and sulfate ions in Kuwait. Although their description of the pits resembled that of Type 1 1/2 pitting corrosion, they did not look for or observe the presence of a biofilm. Instead, they proposed yet another mechanism that involved attack of the protective cuprous oxide film along grain boundaries by chloride ions.

III. DESCRIPTION OF PITTING CORROSION OF COPPER IN INSTITUTIONAL WATER SYSTEMS

A. Saudi Arabia Hospital Study

An unusual type of pitting corrosion of copper tubing was reported in a hospital in Saudi Arabia. There were significant differences in the occurrence of pitting in sections of the hospital piping system that received water from different sources. The unusual type of pitting was most prevalent in pipe sections of the hospital that contained warm water. Although no microbiological studies were performed on failed tubing from this system, PAS-positive material was recovered from the pipe wall.
B. Corrosion Characteristics of German Hospital Copper Water Lines

Pitting corrosion similar to that observed in Saudi Arabia and from a hospital in eastern Scotland was reported in a hospital in Germany shortly after it had opened in 1986.9 Approximately one third of the water system exhibited failures. Coincident with the pitting phenomena was a temporary and locally high concentration of dissolved copper ions and solid copper corrosion products in the water. Problems occurred with highest frequency in deadleg sections of cold and warm water lines. The tubes contained a deposit of adherent cupric oxide and showed pitting under mounds of basic cupric sulfate with loose powdery cuprous oxide inside, on top of, and around the perimeter of the pit.

Chemical analysis of the corrosion products revealed copper complexes with organic compounds of microbial origin such as pyruvate, lactate, and histidine.15 A biofilm was detected and found to contain polysaccharides, oligopeptides, and n-acetylated derivatives of glucose, mannose, and galactose. Extended absorption fine structure spectroscopy detected Cu\(^{1+}\) complexes with imidazole residues of histidine in the biofilm.16

Microbiological evaluation of the corrosion deposits recovered from a county hospital in Germany was carried out by Wagner et al.10,13 The presence of high numbers of surface-associated bacteria was not always correlated with pitting. The range of culturable bacterial species was quite variable even among the pitted pipe samples, indicating that one species was not responsible for all the observed pitting corrosion. Nevertheless, three isolates were consistently recovered: two strains of *Pseudomonas paucimobilis*, each with different pigmentation, and *P. solanacearum*.11 Whereas all three isolates were capable of growth as suspended cultures at temperatures as high as 40°C, one strain of *P. paucimobilis*, when grown in a mixed-population biofilm, tolerated temperatures of 50°C.11 The isolate of *P. solanacearum* was found to be a facultative anaerobe capable of nitrate respiration to dinitrogen and capable of producing large quantities of uronic acid-containing exopolysaccharide which was enhanced at elevated temperatures. The three isolates displayed copper tolerance, particularly at elevated temperatures which coincided with enhanced exopolysaccharide production.16 Thus, there may be a relationship between temperature, exopolysaccharide production, copper tolerance, and pitting corrosion. Additional research needs to be carried out to establish any correlation between these factors.

Water that had passed through the water distribution system of the hospital was run through test loops of copper tube.10,13 After 2 years, the manifestations of pitting and generalized corrosion were reproduced, although at a slower rate than was observed previously in the hospital piping system. A black layer of cupric oxide developed on the surface.
of the tubing, tubercles of malachite or posniakite were observed, and both uniform attack and pitting attack occurred at the same time. Unlike the tubing in the hospital water distribution system, no continuous biofilm was recovered from the tubing in the test loop. Thus, simulation of the unusual corrosion reaction has been achieved, but at a slower rate and without evidence of a biofilm.

C. Corrosion Characteristics of Facilities in Southwest England

Detailed examination of copper tubing that suffered from the unusual types of pitting corrosion in two hospitals in southwest England revealed failures with characteristics similar to those in Germany, Saudi Arabia, and Scotland. Pitting was associated almost exclusively with pipes bearing black cupric oxide films containing a microbial polymer biofilm. The pitted pipes were invariably from locations where ambient temperatures were 30 to 40°C and where water flow rates were low or intermittent, or in some instances stagnant. The water sources for the two hospitals in southwest England which experienced the unusual type of pitting corrosion were obtained from different rivers. The water was soft with high humic acid content.

A study was conducted to relate bacterial densities with pitting using 14 pipe samples collected from the two hospitals that experienced the unusual pitting corrosion, as well as a third hospital in the region that did not experience the unusual type of corrosion. No SRB were detected in any of the samples based on anaerobic incubation in Postgate C medium at 30°C for 3 to 5 d. Twelve isolates were identified by the API 20NE system as falling into one of the three following genera: Methylobacterium, Pseudomonas, and Aeromonas. All samples examined had some bacteria present. The unusual type of pitting corrosion, as determined by the presence of perforations, well-developed pits, and black cupric oxide over the majority of the surface, occurred only where bacterial densities exceeded 100-colony forming units (cfu)/ml. In some cases, pitting was observed where bacterial densities were low, but polysaccharide abundance was high, based on PAS base staining.

D. Hospital Survey in Southwest Scotland

Severe pitting corrosion has been reported in several hospitals in southwest Scotland. In one hospital alone, 64 failures were reported between 1982 to 1988. Angell et al. reported a pepper pot pitting on the tube surface that exhibited some of the features of the unusual type of pitting corrosion reported in the other hospitals described above. Tubes contained a film that stained PAS- and alcian-positive, suggesting the presence of substituted and unsubstituted polysaccharides. A superficial
deposit of organic material was also detected that was thought to be composed of humic substances. Examination of the pitted areas from which the corrosion product mound had largely detached revealed a copper (I) oxide layer with a number of pepper pot holes in it. The perforations in the cuprous oxide layer of these pits were larger than those associated with the pits in tubing from the hospitals in Germany, Saudi Arabia, and southwest England (Figure 2). A short distance from the pit, a deposit of cuprous oxide was observed beneath a layer containing spherical cupric oxide nodules and biofilm. McEvoy and Colbourne found that more severely corroded tubes contained a more fully developed biofilm. Microbiological analysis of the black tubercles covering the perforated areas indicated the presence of SRB and a variety of aerobes, including Pseudomonas and Alcaligenes spp., pink-pigmented facultatively methylotrophic bacteria, and fungi. By contrast, fewer and much smaller black nodules were observed in the tubing taken from hospitals that had not experienced pitting corrosion. No pitting was observed in tubing with thin biofilms containing fewer rod- and cocci-shaped bacteria.

IV. FACTORS CONTRIBUTING TO MICROBIALLY INFLUENCED PITTING CORROSION OF COPPER TUBING

A. Temperature

Substandard water maintenance was thought to contribute to the corrosion problems. The institutional buildings experiencing pitting corrosion had a lower temperature in their hot water systems than those without corrosion. Practical experience has shown that MIC has not been a problem in water systems maintained above 60°C. Studies by Walker et al. showed that the hot water in the hospitals which experienced the pitting corrosion was not maintained at a sufficiently high temperature to inhibit microbial growth. Most of the time the temperature was below 50°C, which enabled the bacteria to proliferate. A two-stage continuous culture model was used to mimic the corrosive environment of one of the hospitals. Using a microbial inoculum from the corroded copper tubing, these authors showed that the biofilm could be established at temperatures up to 55°C. However, at temperatures above 55°C the biofilm was greatly reduced. That pitting corrosion and biofilm accumulation were much more pronounced at temperatures below 55°C than above that temperature suggests the involvement of a biological rather than a nonbiological reaction. It was concluded that the temperature of the hot water supply has a significant role in the control of MIC in these institutional buildings.
B. Water Chemistry

Although the quality of the supply water was considered to be good, the level of assimilable organic carbon (AOC) was found to be higher than in other areas where corrosion problems were absent. The water in hospitals which did not maintain their hot water above 50°C exhibited higher AOC, presumably due to sloughing of biofilm from the walls of the tubing. In this respect, the growth of biofilm microorganisms on the walls of the piping can lead to the degradation of water quality. Besides serving as nutrients for the bacteria, some of the organic carbon (i.e., humic substances in the supply water) are strong chelators of copper and counteract the bactericidal properties of copper ions in solution. Aluminum-chelating phenolic material was recovered from the biofilm/corrosion deposits.35

Dissolved oxygen concentration in the water of hospitals experiencing corrosion dropped to 0.1 mg/l during the 11-h period that hospital activities were minimal (between 7 p.m. and 6 a.m.). This drop was believed to be due to the respiratory activities of the biofilm bacteria, since the planktonic bacterial densities were not high enough to account for the oxygen demand. The establishment of anaerobic conditions was thought to promote the growth of SRB which were found in the biofilm and may have contributed to the corrosion reactions.

The supply water also contained fine particulates which accumulated in the storage tanks and promoted microbial growth. A combination of the factors identified above were thought to promote the extensive biofilm growth on the inner pipe surface and contribute to the pitting of the underlying copper surface. Although a specific mechanism was not identified for the microbial role in the corrosion process, it was felt that removal of the humic substances from the water, increasing the water temperature to 55 to 60°C, and a general cleanup of the system was needed to control the corrosion problem. Unfortunately, once this type of corrosion is allowed to start, it is difficult to control.

C. Design and Installation

In addition to water characteristics and temperature, plumbing design and installation seem to play a significant role in system susceptibility to MIC.8 Stagnation of water can occur through the existence of deadlegs built into the system. These regions are particularly vulnerable to microbial accumulation and are difficult to treat. Stagnation also occurs when water is left in the system for extended periods of time following pressure testing before the system goes into operation. Systems designed with long horizontal runs of tubing are susceptible to MIC. This feature
promotes the accumulation of sediment on the bottom of the tubing, which increases the surface area for microbial colonization and growth and promotes the development of anaerobic conditions in these areas which are conducive for the growth of SRB and other potentially corrosive anaerobic species. Inadequate filtration of source water can also lead to sediment accumulation in various parts of the system. Poor soldering practices can lead to the accumulation of a bead on the inside of the tubing at joints. This irregularity in surface contour has long been known to produce eddies in the water flow pattern and promote erosion corrosion that is free of deposits of any kind. The protruding bead also acts to entrain bacterial cells that accumulate as a biofilm in the eddies.

V. LABORATORY SIMULATIONS OF MICROBIALLY INFLUENCED CORROSION OF COPPER

A. Attempts to Reproduce Unusual Type of Pitting Corrosion Observed in the Field

Controlled laboratory studies were carried out to determine whether the three bacterial isolates recovered from the corroded tubing in the German hospital, when grown as a mixed population in a synthetic water, could reproduce the pitting corrosion of copper observed in the field. Flow-through reactors containing copper rings exposed to synthetic water with a chemistry similar to that used by several of the hospitals described above that experienced the unusual type of pitting corrosion were operated in the presence and absence of bacteria and the corrosion rates compared after 5 months. The copper surfaces exposed to these conditions exhibited none of the features of the pitted copper tubes recovered from the hospitals, although there were important differences between the materials recovered from the sterile and inoculated reactors. The sterile copper surfaces exhibited slight superficial corrosion with a basic cupric carbonate deposit. The remainder of the surface contained a cuprous oxide film. On the outer edge of the copper ring a pit was observed which contained crystalline cuprous oxide.

The rings from the inoculated reactor contained a biofilm with polysaccharide. Corrosion was observed over a broad area, producing an orange layer of cuprous oxide and in some places a more coherent cuprous oxide film surrounded by deposits of basic copper carbonate and sulfate crystals. In other areas of the ring pits containing loose copper oxide were observed under basic copper carbonate deposits. A film of black cupric oxide occupied areas surrounding the pits. Although this laboratory study failed to reproduce the spherical nodules of cupric oxide characteristic of the unusual type of pitting observed in the hospitals described above, pitting was observed in the presence of polysaccharide-producing bacterial biofilms.
B. FTIR Studies

Sensitive analytical techniques have been developed to study MIC of copper in real time, in a nondestructive manner, and without disturbance to the system. Bremer and Geesey\(^1\) demonstrated that bacteria isolated from pits in corroded copper tubing removed from a heat exchanger could be grown either as a batch culture or as a continuous culture on a germanium internal reflection element (IRE) and monitored by attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR) for up to 417 h (Figure 3). The spectra revealed the accumulation of microbial products over time at the surface of the IRE. These products consisted largely of protein and polysaccharide as well as other unidentified components. Operation in the double beam mode using a sterile IRE exposed to a sterile liquid bacterial culture medium allowed accurate subtraction of components from the bulk aqueous phase that had adsorbed to the surface of the inoculated IRE (Figure 4).

ATR/FTIR was adapted for MIC studies of copper by depositing ultrathin films of copper on the IRE (Figure 5).\(^2\) Copper films of 6 to 7 nm nominal thickness, when deposited by vapor deposition, appeared to be continuous based on X-ray photoelectron spectroscopic analysis and contained a cuprous oxide layer at the surface. Atomic force microscopic evaluation of the copper thin films revealed them to be coalescing aggregates of copper atoms (Figure 6). When IREs coated with 6- to 7-nm-thick films were submerged in an aqueous medium, there was sufficient transmission of IR radiation through the Cu to obtain significant water absorbance at 1640 cm\(^{-1}\). The intensity of the water absorption band was found to be very sensitive to changes in thickness of the copper film.\(^2\)\(^-\)\(^4\) This feature can be used to study the effect of microbial biofilms and their products on the integrity of the oxidized copper surfaces in aqueous environments.

One strain of *P. paucimobilis*, recovered from the corroded copper tubing in the German hospital, when grown as a biofilm on thin films of copper on Ge IREs, promoted higher rates of copper corrosion than sterile controls subjected to otherwise similar conditions.\(^1\)\(^7\) That attached bacteria and not suspended bacterial cells promoted the observed deterioration of the copper film was demonstrated by flow-through studies. After an initial inoculation to initiate biofilm development on the copper film, no additional bacteria were added to the aqueous medium flowing over the surface. Corrosion occurred only after biofilm had developed.\(^1\)\(^7\) These results suggest that pure cultures of bacteria isolated from pitted copper tubing can destabilize copper under highly controlled laboratory conditions.

Several bacteria were isolated from corrosion deposits on copper tubing exposed to tap water from laboratory faucets at California State University, Long Beach, and used to study the MIC of copper. One
FIGURE 3. Infrared spectra collected at various times after inoculation of bacterial isolate CCI#8 in an ATR cell containing a Cu-coated germanium IRE.
FIGURE 4. Schematic diagram of the optical bench of an FTIR spectrometer containing two cylindrical ATR cells operated in the dual beam mode.

FIGURE 5. Schematic diagram of a copper-coated germanium IRE exposed to flowing medium inoculated with film-forming bacteria.
isolate, referred to as CCI#8, when exposed to a copper-coated IRE in stagnant culture media, produced an immediate decrease in the stability of the copper film based on changes in the intensity of the water absorbance band.\textsuperscript{25} When this experiment was repeated with another bacterial isolate (CCI#11), the copper film remained stable in the presence of this bacterium over a 77-h period. These studies suggest that some, but not all, bacteria promote deterioration of copper thin films.

A similar study was performed in a flow-controlled sampling cell.\textsuperscript{25} When CCI#8 was inoculated into the flowing medium that passed over the copper film, very little deterioration of the metal was observed over a 2.5-h period. Unlike the static culture experiment described above, no change in the stability of the copper film was observed after flow was suspended and the sampling cell was maintained as a static culture. However, when flow was resumed after 64 h as a static culture, there was an immediate loss of film stability. There was visual evidence of a biofilm on the inoculated IRE and localized deterioration of the copper
film under the biofilm. No bacterial growth or deterioration of the copper film was observed in the sampling cell that was maintained as a sterile control under the same flow regime. The results suggest that flow conditions influence biofilm-induced deterioration of the copper film and that in the absence of bacteria, flow has little or no effect over the range of flow conditions tested in these experiments. It should be noted that flow conditions have been shown to affect copper corrosion without the assistance of microorganisms.

The experiments described above were rerun over a longer time period under different flow regimes to obtain a better understanding of the relationship between flow, biofilm growth, and deterioration of the copper film. Exposure of the copper thin film to CCl#8 under flowing conditions for 330 h resulted in only slight deterioration of the metal. This corresponded to a corrosion rate of $8.4 \times 10^{-4}$ mpy. Shortly after flow was stopped, the corrosion rate increased to $8.8 \times 10^{-3}$ mpy. These rates represent the average corrosion rate over the entire IRE and not where focused attack occurred under portions of the biofilm.

At the same time that the copper film deteriorated there was an increase in the amount of exopolysaccharide that accumulated on the surface. No increase in accumulation of other cell components such as protein was observed during this time. The accumulation of biofilm on the copper-coated IRE was confirmed by visual examination and plating of homogenized biofilm at the termination of the experiment. Again, the area under the biofilm was discolored, verifying the copper deterioration detected by the FTIR. The data confirm earlier studies that changes in flow rate and allowing the system to become stagnant promote biofilm-induced copper corrosion.

Some bacterial biofilms protect copper from the destructive action of other bacteria. Biofilms of CCI#11, grown under flowing or quiescent conditions, caused no detectable deterioration of the copper film, even over exposure periods of up to 500 h. Once established, biofilms of CCI#11 protected the copper film from attack by CCI#8 over a 300-h period under flowing or quiescent conditions. Protection was not due to exclusion of CCI#8 from the surface by the biofilm of CCI#11, since changes in the infrared spectrum of the biofilm were observed after inoculation of CCI#8 to the system and approximately equal numbers of both bacterial types were recovered after plating samples of the biofilm on solid culture medium after termination of the experiment. These results demonstrate for the first time that a particular type of bacterium can protect the surface of copper from the aggressive localized attack of another type of bacterium. Since biofilms are present on most surfaces submerged in aqueous environments and only a very small fraction of these surfaces are subject to pitting corrosion, it is not unreasonable to suggest that some bacteria play a protective role in MIC of copper tubing.
C. Role of Microbial Exopolysaccharides in Localized MIC of Copper

Studies by Fischer et al.\textsuperscript{3} and Paradies et al.\textsuperscript{15} indicated that polysaccharides and oligopeptides were associated with corrosive biofilms. Exopolysaccharides isolated from biofilm bacteria have been shown to destabilize copper thin films. When a copper-coated IRE was exposed to a 1\% solution of a crude acidic exopolymer from a sediment bacterium (FRI), the copper film corroded immediately.\textsuperscript{28} A similar phenomenon was observed when the copper-coated IRE was exposed to a suspension of other acidic polysaccharides such as alginic acid and gum arabic.\textsuperscript{24} The results suggest that metallic copper is sensitive to a wide range of acidic polysaccharides, including those produced by some biofilm-forming bacteria that colonize copper tube.

Results from several studies suggest that the metallic copper is oxidized by acidic polysaccharides. X-ray photoelectron spectroscopy has shown that some of the copper deposited on the IRE after exposure to gum arabic and alginic acid was oxidized to Cu\textsuperscript{2+}, that which was exposed to other bacterial polysaccharides was oxidized to Cu\textsuperscript{1+}, and that which was exposed to yet other types of bacterial exopolysaccharides underwent little oxidation and remained as Cu\textsuperscript{0} (Figure 7).\textsuperscript{29-30} These results are consistent with a corrosion mechanism based on a copper concentration cell formed by the excretion of exopolysaccharides with
different affinities for copper ions by different bacterial species within a biofilm.\textsuperscript{31-32}

Paradies et al.\textsuperscript{8} presented evidence that the imidazole or L-histidine groups of the oligopeptide chains in biofilms participate in complex formation with Cu\textsuperscript{2+}. These authors also have detected a Cu\textsuperscript{3+} complex in corrosive biofilms which was formed through a reaction with peroxide. A corrosion mechanism involving these complexes has been proposed.

The chemistry and possibly the structure of exopolysaccharides of copper-corroding bacteria are influenced by the presence of copper in the surrounding environment. Bremer and Geesey\textsuperscript{33} demonstrated that the copper-complexing carboxyl groups contributed by uronic acid subunits are significantly more abundant in exopolysaccharides produced by cells exposed to copper than those produced in environments with little or no copper present. The exopolymer produced in the presence of copper bound approximately 16\% of its weight in copper. It is likely that some microorganisms produce large amounts of copper-complexing exopolymers to protect themselves from the toxic effects that Cu\textsuperscript{2+} has on essential reactions inside the cell. These polymers accumulate during biofilm growth in a heterogeneous manner over the surface. This heterogeneity may promote localized dissolution of metallic copper, which takes the form of pitting. Whether pitting propensity is simply related to the quantity of exopolymer produced or a reflection of subtle differences in exopolymer chemistry or structure remains to be determined. Further research will be required to gain a more complete understanding of the role of specific bacterial exopolymers in pitting corrosion of copper. Nevertheless, significant progress has been made in demonstrating the participation of microbial biofilms in this phenomenon.

VI. PREVENTION OF MIC OF COPPER TUBING USED IN POTABLE WATER SYSTEMS

Based on the information presented above, it appears that a combination of factors contribute to the unusual forms of pitting corrosion of copper tube in institutional buildings such as hospitals. These factors include the use of soft water with low pH, high suspended solids, and AOC content, long-term or periodic stagnation of water in the pipeworks which produces widely fluctuating oxygen concentrations, maintaining water temperatures that promote rapid growth and activity of naturally occurring bacteria that form biofilms on the pipe wall, and the lack of an adequate monitoring program to periodically evaluate water quality and pipe wall condition. Thus, it should be possible to avoid the undesirable corrosion by identifying and specifying limits for these parameters.
Nutall and Rich\textsuperscript{36} described the key factors for design, installation, and commissioning of copper plumbing systems in large public buildings. From a microbiological point of view, they were concerned more with control of \textit{Legionella pneumophila} than of corrosion-causing microorganisms, since there was little information available on MIC of copper tube at that time. More recently, Fischer et al.\textsuperscript{9} have summarized many of the precautions that should be followed when water chemistry, temperature, and system operation predispose the system to MIC. Based on these previous reports and the studies described above, a number of recommendations can be made that reduce the likelihood of microbiologically induced pitting corrosion of copper tubing. The recommendations fall into three categories: system design, installation, and operation.

The system should be designed to minimize the possibility of water stagnation. Deadlegs (sections of tubing which contain stagnant water for long periods of time without being refreshed in any way) should be eliminated. In large installations, pumps should be installed that maintain water flow velocities between 0.7 to 1.5 m/s at all times. Filtration equipment may be desirable for removal of suspended particulates in the source water that could accumulate along horizontal runs of plumbing.

Although little attention has been given to monitoring programs, periodic examination of the interior pipe wall surface for deposit accumulation, tubercle formation, and biofouling permits recognition of a potential MIC problem and initiation of corrective action before control over the problem is lost. Monitoring of this nature requires installation of removable, replaceable pipe sections at different locations in the system, periodic inspections, and a plan of corrective action when MIC is observed. This alternative could be less costly than replacement of all failed tubing in a system that is particularly prone to MIC.

Installation of the plumbing system should be carried out according to copper tube manufacturers' recommended procedures. Soldered joints should be smooth and free of solder beads on the inside pipe surface. Debris introduced into the tubing during installation should be removed before pressure testing. No water should be introduced into the system for pressure testing or for other reasons until it is certain that the system can be operated under the conditions for which it was designed soon after testing has been completed. The system should never be allowed to go out of operation without draining all of the water. Only high-quality water should be used during pressure testing. If there is a delay between the time the system is pressure tested and put into commission, water should be circulated through all wetted tubing at regular intervals to prevent stagnation. Immediately prior to commissioning, the system should be sterilized to kill any harmful microorganisms that inadvertently entered the system during previous operations.
Operating conditions should be based on health-related, microbiological standards applicable to potable water systems. The use of high-quality water is strongly recommended. Water hardness should be adjusted to establish a protective oxide film on the inner surface of the plumbing material. Of all the recommendations made, maintaining proper water temperature in the lines is the most important for minimizing MIC. Water temperature should be maintained below 25°C for cold water and above 55°C for hot water at all times. Maintenance of these temperatures may require water flow through the pipes at regular intervals.

In summary, certain water chemistry, system design, and installation and operation practices predispose copper tubing to microbiologically induced pitting corrosion which results in through-wall perforations that are costly to repair. The phenomenon appears to be related to a combination of chemical and biological factors which act in concert to cause the observed failures in institutional buildings. By altering several of these factors at the same time, it should be possible to reduce or eliminate the problem.

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