

Corrosion of copper pipes has been associated with waters with high pH and low alkalinity that also contain significant levels of chloride and sulfate. This study systematically evaluated the effect of pH, alkalinity (or dissolved inorganic carbon [DIC]), orthophosphate, and sulfate on the nature of copper corrosion using a pilot-scale experimental pipe loop system. Experiments were conducted in the absence of silica, aluminum, or organic carbon, which previously have been linked to pitting corrosion in drinking water systems, and all test waters contained moderate levels of chloride. The study also investigated the effect of chlorine concentration and form of chlorine on copper-pitting corrosion. Results showed that pitting corrosion of copper pipes was reproduced in the pilot-scale systems after only 91 days of operation. Pitting corrosion occurred in water with low chlorine concentration and DIC and in pH 9 water in the presence of chloride. Pitting was not observed at pH 6.5 and 7 and was evident at pH 8 only when higher chlorine levels were maintained. Sulfate was not necessary to develop pitting corrosion; however, it did affect the composition of the corrosion by-products.

Pitting corrosion of copper in waters with high pH and low alkalinity

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Localized corrosion of copper pipes, or “pitting” corrosion, is a major cause of household plumbing failure. In relatively short periods of time after installation of copper plumbing, copper pitting can lead to pipe failure in the form of pinhole leaks. The cost of plumbing repair and the associated expenses of repairing water-damaged materials can be excessive for property owners. Additionally, pinhole leaks may go undetected in walls or basements for months, providing an environment for the growth of mildew and mold. Many homeowners elect to replace their entire plumbing system to avoid the hassle of continually repairing damage caused by copper pitting even though this may only offer a short-term solution before pinhole leaks in the new plumbing occur.

Despite the nature of copper-pitting corrosion, the extent of the problem may be underreported by water utilities for several reasons. First, because copper-pitting corrosion is typically not associated with a regulatory violation (i.e., violation of copper action level), there is no noncompliance issue to report. Second, water utilities may be threatened by the extent of damage possible, the costs of repair, and the threat of legal action against them. Third, homeowners may not notice pinhole leaks in hidden plumbing, or they may not regularly examine their plumbing. Last, if homeowners do notice a leak, they may be more likely to call a plumber or local point-of-use water treatment system supplier rather than the water utility.

Pitting corrosion of copper plumbing materials in water is poorly understood despite several studies on the topic (Marshall & Edwards, 2005; Harrison et al,

Additional photographs that further illustrate the material discussed in this article can be found in the March 2008 issue of e-Journal AWWA at www.awwa.org/Publications/JournalCurrent.cfm.

2004; Duthil et al, 1996; Edwards et al, 1994a; 1994b; Kasul & Heldt, 1993; Lucey, 1967). Pit initiation has been associated with microbial activity, copper material imperfections, excess carbonaceous manufacturing residues on the pipe surface, water chemistry, stray currents, soldering flux, and other factors. Several water chemistry parameters have been postulated to be responsible for the initiation and propagation of pitting corrosion. The parameters include pH, alkalinity or dissolved inorganic carbon (DIC), chloride, organic carbon, chlorine, aluminum, silica, sulfide, and sulfate.

Reliably establishing the underlying source of a copper pinhole leak problem in a drinking water distribution system is complicated. First, multiple agents—often present simultaneously—have frequently been suggested as causative factors of pitting. Examples of suggested causes are favorable water quality conditions, the presence of solids (e.g., aluminum) on failed copper pipe surfaces, the quality and type of copper pipe, grounding effects, construction methods, workmanship deficiencies, and the presence of bacteria (e.g., sulfate-reducing bacteria) in the distribution system. Second, much of the current understanding of localized copper corrosion in water is based on electrochemical analysis techniques that have not been proven to be predictive or accurate under conditions typically experienced in real distribution systems and/or tests that have been conducted in artificial waters that exaggerate some water quality parameters.

The objective of this study was to investigate the effect of water pH, chloride, sulfate, alkalinity, and orthophosphate on the nature of copper corrosion (i.e., localized and uniform) in extensive copper pipe corrosion experiments conducted under a relatively controlled environment. Organic material, aluminum, silica, and other important water quality parameters that are often linked to copper-pitting corrosion were absent from the test waters. Research was conducted using a pilot-scale recirculating-water copper pipe loop system. A detailed surface analysis was conducted on the physical and chemical nature of copper corrosion in the copper plumbing. Techniques used in this study were powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) in conjunction with SEM, and optical microscopy.

BACKGROUND AND LITERATURE REVIEW

Because copper is resistant to corrosion, easy to install, abundant in nature, and low in cost, the metal is widely used in home plumbing and distribution system piping material. Despite copper's corrosion resistance, however, it is not inert and can experience both uniform and nonuniform or pitting corrosion. Uniform corrosion describes the corrosion of a metal evenly across the surface leading to the relatively uniform deposition of corrosion deposits over the pipe surface. Generally, uniform copper corrosion is favored in waters with low pH and high alkalinity (Ferguson et al, 1996). Pitting corrosion

refers to localized corrosion or corrosion that takes place at isolated points on the copper surface.

Pitting corrosion theories. Pitting corrosion of copper in water has been studied by numerous researchers (Marshall & Edwards, 2005; Harrison et al, 2004; Duthil et al, 1996; Edwards et al, 1994a; 1994b; Kasul & Heldt, 1993; Lucey, 1967). The literature offers several theories to describe copper pit initiation and growth in drinking water systems through chemical reactions. Various studies have associated pit initiation with microbial activity, material imperfections, carbonaceous manufacturing residues on the pipe surface, stray currents, soldering flux, and other factors. As is apparent from these different theories, no single best theory has emerged, and each theory has weaknesses that illustrate the complexity of localized copper corrosion. Some of the discrepancies in these theories may be associated with differences in experimental approaches among electrochemical, bench scale, and full-scale observations. Most likely, pitting has multiple causes, and no single all-encompassing theory would be applicable.

Nonetheless, researchers tend to agree that the most common failure mechanism for copper tubes and pipes arises from a localized breakdown of the thin, protective cuprous oxide film formed on the copper surface. The breakdown can be caused by chemical or mechanical attack, poor deposition of the pipe surface layer, or the presence of nonuniformities in the surface. This thin oxide film normally forms on copper surfaces exposed to potable water and is generally fine-grained, tightly adherent, and highly protective. The oxide film frequently is overlain by thin deposits of basic cupric salts that often enhance the protection, such as hydroxy carbonates, hydroxy sulfates, or hydroxy chlorides. Depending on the relative concentrations of these particular anions and other water quality factors (such as pH), the effects may be either conducive to or ameliorative of pitting corrosion.

Membrane cell theory of copper-pitting corrosion. Lucey (1967) generally is credited with developing the modern framework for the structure and propagation of copper corrosion pits and proposed the membrane cell theory of copper-pitting corrosion that identified the chemical reactions involved in this type of corrosion. The work was based on field observations, bench-scale studies, and electrochemical approaches. Lucey stated that a porous membrane of cuprous oxide (cuprite) is an "essential feature" of a copper corrosion pit and concluded that pitting arises as a result of a deposited cuprous chloride layer between the corroding copper and the membrane.

According to Lucey, the anodic reaction occurs between the cuprite membrane and pipe wall where copper metal is oxidized into cuprous ions. Some of the cuprous ions react with oxygen to form cuprite, which precipitates between the membrane and the pipe wall. The remaining ions pass through the membrane and are further oxidized

into cupric ions. Some of these cupric ions precipitate as insoluble copper salts (i.e., malachite or brochantite), and the remaining ions are cathodically reduced to the cuprous state. This cathodic reaction differs from conventional pitting theory in that the cathode's external cathodic surface is not necessary and no "large-scale" flow of electrons through the metal occurs.

In the past decade, many researchers have continued to investigate and expand on Lucey's research. Some have suggested modifications to his theory, and others have proposed alternative pitting theories. For example, Sosa and colleagues (1999) revisited Lucey's work on cold water pitting by repeating experimental conditions using an electrochemical approach. They showed that currents carried through the bulk metal accounted for more than 80% of the weight loss in the pit. This observation contradicts the membrane cell theory that places the cathode above the anode in location.

Categorization of copper corrosion. Localized copper corrosion in water has been categorized into at least three types of water on the basis of chemistry and physical features: cold water (type 1; Kasul & Heldt, 1993; Cruse & von Franqué, 1985; Cruse & Pomeroy, 1974; Campbell, 1950), hot water (type 2; Mattsson & Fredriksson, 1968), and soft water (type 3; Page et al, 1974). Soft water copper pits are described as being relatively wide and shallow and consist of an exterior layer of brochantite and/or malachite over a layer of crystalline red-brown cuprite and the corroding copper surface. The voluminous corrosion deposits of the exterior layer are released to the water and potentially can even cause water blockage. Waters having low conductivity, low alkalinity, and relatively high pH are typically associated with soft water pitting. Recent research reported on communities in Ohio and Florida that experienced widespread reports of copper plumbing pinhole leaks (Lytle, 2006; 2005). The water quality associated with the problem included high pH, low alkalinity, and significant levels of chloride and sulfate. This water quality most closely fits the characteristics of soft water pitting and has been associated with many other widespread pitting cases investigated by the authors and recently reported by others. Table 1 details the water quality of communities reported to experience various degrees of soft water pitting.

The role of chloride and sulfate in pitting attack. Clearly water chemistry is important with respect to soft water pitting attack. Water prone to soft water pitting attack is characterized by relatively high pH and low alkalinity (i.e., low DIC or bicarbonate concentrations), and sulfate and chloride are nearly always associated in one way or another with all forms of pitting. The relative importance of chloride and sulfate in copper-pitting corrosion is debatable. Several studies have been conducted to evaluate the role of chloride in copper-pitting corrosion (Nishikata et al, 1990; Drogowska et al, 1987; Akkaya & Ambrose, 1985). Historically most theories held that

chloride is the species responsible for pitting (Shalaby et al, 1989; Cornwell et al, 1973; Lucey, 1967). Edwards and colleagues (1994b) concluded that sulfate and nitrate play important roles in pit initiation and development, and these ions may be more critical to copper pitting than chloride is. This was later supported by the work of Duthil and co-workers (1996), who reported on the role of chloride and sulfate in the pitting of copper on the basis of pit germination rates using an electrochemical approach. They showed that either chloride or sulfate can be responsible for copper pitting when either is present by itself in water. When both anions are present, chloride can have either an accelerating or inhibiting effect, depending on the relative concentrations of both sulfate and chloride.

Edwards and colleagues (1994a) investigated the role of chloride and sulfate on copper pitting in water using accelerated corrosion rate experiments. They found that chloride increased copper corrosion rates in the short term. With time, however, chloride actually produced protective surfaces at pH 7.6. Sulfate initially was not aggressive, but corrosion rates increased above those of chloride over time as scale formed. Edwards and co-workers noted that brochantite, $\text{Cu}_4(\text{OH})_6(\text{SO}_4)$, was always present over soft water pits and hypothesized that its formation may be the key to hot water pitting. Thermodynamic calculations showed that brochantite formation was favored over malachite and atacamite in waters having high ratios of sulfate to chloride or sulfate to bicarbonate.

Schmitt and Slavcheva (2001) used an electrochemical noise technique to investigate the effect of chlorides, sulfates, and bicarbonate anions on copper-pitting corrosion. They concluded that sulfate typically has an activating effect, chloride has a passivating effect, and bicarbonate acts as a buffering agent. However, the combination of all three anions in a narrow range of concentrations leads to pitting corrosion.

Marshall and Edwards (2005) investigated the role of aluminum on copper-pitting corrosion in drinking water. They demonstrated that water containing aluminum, high chlorine residual, and relatively high pH caused pinhole leaks in a laboratory setting. Specifically, a chlorine residual goal of 1.5 mg/L at pH 9.2 and 2 mg/L of aluminum hydroxide solids produced conditions that caused pinhole leaks. In addition, the water had low alkalinity and significant levels of chloride and sulfate, putting it in the broad category of soft water pitting corrosion (Table 1). However, they reported that no pitting was observed in the absence of aluminum.

Several researchers have proposed theories on how levels of chloride, sulfate, and/or alkalinity in water influence the nature of copper minerals that are often associated with localized copper corrosion and affect the protective nature of the cuprous oxide layer (Harrison et al, 2004; Mankowski et al, 1997; Feng et al, 1996a; 1996b; Shreir et al, 1994). Proper identification of these solids is particularly useful in understanding pitting mechanisms

TABLE 1 Water quality associated with soft water pitting of copper

Sample Description	pH	SO ₄ ²⁻ mg/L	Cl ⁻ mg/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Total Alkalinity mg/L as CaCO ₃	DIC mg/L C	TDS mg/L	Other	Reported Factors	Reference
Ohio water	8.65	95	30	22	19	20	4.7	200		High chloride and sulfate relative to alkalinity	Johnson et al, 2006
Synthetic water	8	40	NA	40	NA	80	9.8	NA	300 mg/L aluminum solids	Combination of free chlorine and aluminum solids, flow rate	Rushing & Edwards, 2004
Synthetic water	9.2	15	20	17	NA	34	7.6	NA	2 mg/L aluminum solids	Combination of free chlorine and aluminum solids at high pH	Marshall & Edwards, 2005
Synthetic water	7.92	38	163	49	19	52	12.8	NA	Hot water	Hot water, low alkalinity, and free chlorine	Fuijeh et al, 1984
United Kingdom water	9.2	35	16	16	3	24	5.4	90		NS	Gilbert, 1966
United Kingdom water	7.8	NA	20	13–15	NA	39–53	9.4	78		NS	Gilbert, 1966
United Kingdom water	7.8–8.2	21–27	14	15	8	26–31	6.3–7.7	87–107		NS	Gilbert, 1966
United Kingdom water	7.6	NA	13	NA	NA	25	6.4	68		NS	Gilbert, 1966
Lime-soda softened surface supply	8.5	150	18	100 ppm total hardness	NA	30	7.1	NA		NS	Hatch, 1961
Ohio water	9.1–9.3	112	NA	25	NA	30–35	6.6–8.0	NA		Low alkalinity	Lytle, 2005
South Dakota water	8.85	368	NA	46	28	54	12.6	NA		NS	Lytle, 2006
Ohio water	8.8	120	64	27	27	39	9	NA		Low alkalinity, SRB	Lytle, 2006
Florida water	8.1	169	47	43	20	46	11	NA		SRB, aluminum solids	Lytle, 2006
Auckland, New Zealand, water	7.1–8.6	6–15	9–18	4–12	12–29	14–35	3.3–9.8	55–100		Silica gel, deposits	Page et al, 1974
Kuwait tap water	8.1	75	52	24	8	12.5	3	NA		NS	Al-Kharafi et al, 1998

Ca—calcium, CaCO₃—calcium carbonate, Cl⁻—chloride ion, DIC—dissolved inorganic carbon, Mg—magnesium, NA—not available, NS—not specified, SO₄²⁻—sulfate ion, SRB—sulfate-reducing bacteria, TDS—total dissolved solids

DIC was calculated from alkalinity and pH.

and the conditions within the pit. Unfortunately, many previous studies did not apply appropriate analysis approaches, and their descriptions of the nature of these solids have largely been speculative. In addition, appropriate thermodynamic analyses and evaluations of redox-sensitive relationships were rarely computed or performed, even semi-quantitatively, to validate the interpretations proposed.

In summary, numerous observations and research findings show that chloride and sulfate are important in pitting corrosion of copper in water. The roles of each ion can differ and cause difficulty when broad conclusions are drawn with regard to copper pitting and corrosion. Further complicating matters, pH, alkalinity, and possibly other parameters (such as aluminum) may also be particularly important with regard to soft water pitting.

MATERIALS AND METHODS

Experimental system design and operation. Experimental systems were designed, constructed, and operated by the US Environmental Protection Agency (USEPA) Water Supply and Water Resources Division in the early 1990s to study the effect of water chemistry on copper(II) [Cu(II)] equilibrium solubility in water (Schock et al, 1995). Copper pipe recirculation experiments specifically have been performed to examine the effect of pH, silica, orthophosphate, sulfate, DIC, and other parameters on Cu(II) solubility in water in a controlled environment. The experimental systems used in this work are patterned after those originally developed for USEPA asbestos-cement pipe studies and some experiments on lead and galvanized pipe corrosion (Schock & Wagner, 1985). However, several important modifications were made.

The most significant modification to the original system design was the replacement of the stainless-steel tanks with 200-L (53-gal) heavy-duty polyethylene tanks. All parts of the recirculation system connection plumbing were made of polyvinyl chloride plastic or transparent vinyl plastic. A magnetic-drive centrifugal pump continually circulated water through the 1.2-m (4-ft) length of 1.27-cm (0.5-in) inner diameter type M hard-drawn copper piping (0.71-mm wall thickness) at a rate of approximately 3,785 L/day (1,000 gpd). The pipe sections mounted in the recirculation systems were chemically cleaned before the start of the experimental runs by the same procedure described elsewhere for the coupons and pipes used in the single-pass pipe loop systems (Schock et al, 1995).

Test water was synthesized by weighing desired levels of appropriate chemicals into water that had passed a mixed-bed deionized water to achieve desired chemistry. DIC was adjusted at the beginning of the run with sodium bicarbonate (NaHCO_3). Chemical additions were made using analytical reagent-grade chemicals. DIC, calcium, and potassium were added using NaHCO_3 , calcium chloride (CaCl_2), and potassium chloride (KCl), respectively, to maintain a consistent background mineral content. Orthophosphate was added as sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$). The pH was adjusted with 6N hydrochloric acid (HCl) or sodium hydroxide (NaOH), which resulted in rising levels of chloride ion (Cl^-) or sodium ion over time. Free chlorine residual was first obtained using sodium hypochlorite (NaClO) solution in most experiments, but in later experiments chlorine was added by saturating deionized water with chlorine gas. Chlorine gas was used to avoid the buildup of chlorate ion with prolonged hypochlorite addition.

As a result of maintaining free chlorine, chloride levels gradually increased over time during the experimental runs, which explained any variability in the chloride levels across experimental runs. Free chlorine was maintained during test runs as high or low concentrations. The goal of high chlorine runs was to consistently maintain free chlorine residual in the tanks between 0.5 and 1 mg/L Cl_2 . Low chlorine runs attempted to maintain a free chlorine residual > 0.05 mg/L Cl_2 . Free chlorine levels reported in Table 2 represent concentrations measured at the time of weekly copper sampling and do not necessarily reflect average weekly chlorine levels or distinctions between high and low chlorine concentration targets. The pH was generally stable but was adjusted (as necessary) once per week when samples were collected for metals and DIC analysis. The pH of the tanks was controlled within ± 0.1 pH of the weekly target value but was usually found to be within ± 0.05 pH. Some absorption of carbon dioxide from the air occurred in the low DIC experiments, even with the floating lids. Chlorine residual adjustments were frequently needed multiple times during the week, depending on the corrosiveness

of the water and the target level for the maintenance of the residual.

Complete water analyses were performed on water samples weekly. Initially, filtration through a 0.1- μm polycarbonate filter membrane with all-plastic syringe apparatus was performed once per month. The filtration procedure was the same as that described previously for lead studies except that the volume was reduced to conserve water (Schock & Gardels, 1983). The soluble metal concentrations were essentially identical within analytical precision from the unfiltered samples in all cases. In later experiments, filtrations were performed every two or three weeks using 0.1- μm nylon syringe filters that had been pretested to ensure minimal loss of dissolved copper. Table 2 summarizes the general background water quality for all relevant experimental runs.

Analytical methods. The pH was measured using a series of benchtop pH/ion-selective electrode meters under computer control to report stability. Measurements of pH used a closed-system technique with repetitive re-equilibrations following the technique of Schock and co-workers (1980). The pH instrument was standardized daily using a two- or three-point calibration with pH 4, 7, and 10 high-precision standard solutions.¹ Dissolved oxygen (DO) was measured with a DO meter² and DO probe.³ Total phosphorus, silicon, calcium, sulfur (sulfate), and copper were measured with a purged inductively coupled argon plasma spectrometer.⁴ Chloride was analyzed using an automated potentiometric titration approach according to method 4500-Cl-D (*Standard Methods*, 1995). Free chlorine was analyzed according to the Hach DPD colorimetric method (*Standard Methods*, 1995). DIC was analyzed by a coulometric procedure on a carbon dioxide coulometer⁵ with acidification module⁶ operated under computer control, equivalent to method D513-02, B (ASTM, 2002). Enhancements in sample gas stripping and sample handling were implemented to improve analytical speed and accuracy.

Other materials. Glassware (excluding pipettes) used for the preparation of standards and solutions were cleaned using a minimum 24-h soak in 5% solution of rinsable detergent.⁷ All glassware was then thoroughly rinsed with a 1:1 HCl or 1:4 mixture of nitric acid (HNO_3) to sulfuric acid (H_2SO_4), followed by deionized water. Reused glassware was immediately cleaned by soaking in 10% volume per volume concentrated HNO_3 and rinsed with distilled deionized water. Glass pipettes were cleaned by soaking them for at least nine hours in a 5% detergent solution,⁷ followed by rinsing with dilute analytical reagent-grade HCl in a plastic pipette washer. A minimum of eight total volumes of deionized water were cycled through the pipette washer as a final rinse. Air displacement micropipettes with disposable tips were used for handling and transferring solutions for tank chemical control.

TABLE 2 Water chemistry of test samples

Run	Run Length days	Parameter— <i>average ± standard deviation (number of samples)</i>								Temperature °C
		pH	DIC mg/L C	Free Chlorine mg/L	Chloride mg/L	Chlorate mg/L	Sulfate mg/L	Calcium mg/L	Ortho-phosphate mg/L	
1	286	7.02 ± 0.05 (42)	10.37 ± 2.17 (82)	0.63 ± 0.27 (42)	60.4 ± 16.9 (43)	3.93 ± 1.39 (42)	0.10 ± 0.06 (28)	4.68 ± 0.18 (43)		22.6 ± 1.0 (42)
2	286	7.00 ± 0.06 (42)	9.92 ± 0.35 (82)	0.65 ± 0.23 (42)	65.5 ± 15.1 (43)	5.62 ± 1.67 (42)	4.77 ± 0.21 (40)	4.34 ± 0.11 (42)		22.8 ± 1.0 (42)
3	286	6.99 ± 0.05 (42)	10.17 ± 0.40 (82)	0.63 ± 0.24 (42)	62.4 ± 14.0 (43)	5.42 ± 1.65 (42)	51.46 ± 1.98 (41)	4.35 ± 0.10 (43)		22.9 ± 1.0 (42)
4	286	7.00 ± 0.05 (42)	9.78 ± 0.38 (79)	0.60 ± 0.37 (42)	61.8 ± 17.7 (43)	4.40 ± 1.68 (42)	153.21 ± 7.19 (42)	4.41 ± 0.14 (43)		23.0 ± 0.8 (42)
5	210	7.98 ± 0.04 (31)	10.55 ± 0.64 (62)	0.56 ± 0.32 (31)	55.5 ± 26.1 (31)	5.17 ± 3.34 (31)	0.15 ± 0.22 (21)	3.79 ± 0.27 (31)		23.0 ± 0.6 (31)
6	210	7.99 ± 0.07 (31)	10.40 ± 0.31 (62)	0.59 ± 0.28 (31)	60.3 ± 24.9 (31)	5.17 ± 3.15 (31)	3.93 ± 0.16 (30)	5.00 ± 0.25 (31)		23.2 ± 0.7 (31)
7	210	7.99 ± 0.07 (31)	10.07 ± 0.19 (60)	0.62 ± 0.30 (31)	56.6 ± 22.7 (31)	4.71 ± 2.87 (31)	50.21 ± 1.72 (31)	4.88 ± 0.09 (31)		23.1 ± 0.7 (31)
8	210	7.98 ± 0.06 (31)	10.37 ± 0.38 (62)	0.72 ± 0.26 (31)	52.6 ± 18.9 (31)	3.89 ± 2.35 (30)	148.23 ± 5.60 (31)	4.88 ± 0.11 (31)		23.0 ± 0.8 (31)
9	99	8.98 ± 0.04 (15)	10.76 ± 0.30 (30)	0.65 ± 0.26 (15)	27.6 ± 4.4 (15)	2.10 ± 0.23 (10)	0.09 ± 0.07 (15)	5.32 ± 0.20 (15)		22.9 ± 0.5 (15)
10	99	8.97 ± 0.03 (15)	10.54 ± 0.38 (30)	0.66 ± 0.25 (15)	27.51 ± 4.35 (15)	2.15 ± 0.24 (10)	4.68 ± 0.32 (15)	4.92 ± 0.20 (15)		23.1 ± 0.5 (15)
11	99	8.98 ± 0.03 (15)	10.31 ± 0.33 (29)	0.78 ± 0.18 (15)	25.58 ± 3.76 (15)	1.92 ± 0.18 (10)	47.74 ± 3.42 (15)	4.93 ± 0.31 (15)		23.0 ± 0.5 (15)
12	99	8.98 ± 0.04 (15)	10.34 ± 0.32 (30)	0.81 ± 0.19 (15)	22.64 ± 2.47 (15)	1.36 ± 0.16 (10)	143.47 ± 11.64 (15)	5.04 ± 0.40 (15)		22.8 ± 0.5 (15)
13	128	6.53 ± 0.03 (19)	9.32 ± 0.34 (37)	0.50 ± 0.26 (19)	37.60 ± 7.58 (19)		0.09 ± 0.05 (19)	4.64 ± 0.06 (19)	2.75 ± 0.08 (18)	24.7 ± 0.5 (19)
14	128	7.07 ± 0.12 (19)	8.83 ± 0.95 (37)	0.73 ± 0.21 (19)	35.32 ± 9.22 (19)		0.09 ± 0.04 (16)	4.79 ± 0.06 (19)	2.85 ± 0.06 (18)	24.8 ± 0.6 (19)
15	128	8.01 ± 0.07 (19)	10.08 ± 0.31 (37)	0.72 ± 0.16 (19)	16.77 ± 3.59 (19)		0.06 ± 0.05 (19)	4.66 ± 0.07 (19)	2.91 ± 0.02 (18)	24.8 ± 0.6 (19)
16	128	8.97 ± 0.07 (19)	10.44 ± 0.55 (36)	0.83 ± 0.19 (19)	15.36 ± 2.82 (19)		0.03 ± 0.04 (19)	4.70 ± 0.08 (19)	2.95 ± 0.02 (18)	24.6 ± 0.6 (19)
17	127	6.52 ± 0.04 (19)	42.24 ± 5.12 (38)	0.26 ± 0.27 (19)	177.45 ± 46.53 (19)		0.07 ± 0.03 (19)	4.61 ± 0.09 (19)	0.04 ± 0.01 (19)	25.1 ± 0.7 (19)
18	127	7.03 ± 0.03 (19)	46.61 ± 1.11 (37)	0.59 ± 0.22 (19)	77.12 ± 17.98 (19)		0.04 ± 0.04 (19)	4.61 ± 0.07 (19)	0.03 ± 0.01 (19)	25.2 ± 0.6 (19)
19	127	7.98 ± 0.10 (19)	48.70 ± 0.79 (38)	0.71 ± 0.21 (19)	35.55 ± 8.97 (19)		0.04 ± 0.03 (19)	4.59 ± 0.07 (19)	0.04 ± 0.01 (19)	25.2 ± 0.6 (19)
20	127	8.99 ± 0.02 (19)	49.17 ± 2.93 (37)	0.49 ± 0.40 (19)	20.60 ± 7.74 (19)		0.04 ± 0.02 (17)	4.59 ± 0.09 (19)	0.03 ± 0.01 (19)	25.2 ± 0.7 (19)
21	91	6.59 ± 0.09 (14)	4.60 ± 0.49 (28)	0.68 ± 0.32 (14)	36.68 ± 6.88 (14)		0.15 ± 0.07 (14)	9.92 ± 0.10 (14)	2.56 ± 0.18 (13)	24.9 ± 0.6 (13)

DIC—dissolved inorganic carbon

Blanks indicate that the parameter was not routinely measured in this run.

Pipe sectioning, photography, and encapsulation. Pipe sections were cut longitudinally with a band saw, and photographs were taken with a digital camera. Areas having defects and pit caps and areas of interest were photographed (3 × magnification). A stereomicroscope with digital camera was used to capture images of areas of interest at 20 × magnification. The pipe section was then

placed on aluminum foil and put in an oven set at 150°F ± 10°F for 15 min. Several grams of epoxy resin⁸ were prepared, and the resin was lightly dabbed onto defects or areas of localized corrosion. Pipes were then placed into a vacuum chamber with the defects facing up, and a vacuum of at least 23 in. of mercury was pulled for 2 min. The vacuum was released to allow the samples to come

TABLE 2 Water chemistry of test samples, *Continued*

Run	Run Length days	Parameter— <i>average ± standard deviation (number of samples)</i>								
		pH	DIC mg/L C	Free Chlorine mg/L	Chloride mg/L	Chlorate mg/L	Sulfate mg/L	Calcium mg/L	Ortho-phosphate mg/L	Temperature °C
22	91	7.07 ± 0.08 (14)	4.87 ± 0.29 (28)	0.80 ± 0.23 (14)	30.60 ± 3.53 (14)		0.10 ± 0.07 (14)	11.60 ± 0.12 (14)	2.80 ± 0.05 (14)	24.9 ± 0.6 (13)
23	91	7.99 ± 0.07 (14)	5.08 ± 0.21 (28)	0.83 ± 0.16 (14)	25.12 ± 1.77 (14)		0.12 ± 0.07 (14)	11.46 ± 0.14 (14)	2.80 ± 0.03 (14)	24.9 ± 0.7 (13)
24	91	8.99 ± 0.07 (14)	5.26 ± 0.26 (26)	0.86 ± 0.18 (14)	24.95 ± 1.27 (14)		0.12 ± 0.09 (14)	11.49 ± 0.20 (14)	2.88 ± 0.02 (14)	24.7 ± 0.8 (13)
25	182	7.06 ± 0.05 (26)	5.06 ± 0.41 (40)	0.41 ± 0.24 (26)	19.88 ± 7.56 (9)		32.85 ± 1.57 (8)	12.49 ± 0.22 (25)	0.01 ± 0.01 (9)	25.6 ± 1.1 (23)
26	182	7.96 ± 0.08 (26)	5.39 ± 0.28 (38)	0.25 ± 0.24 (25)	20.48 ± 9.64 (9)		33.07 ± 0.68 (8)	12.80 ± 0.28 (27)	0.02 ± 0.01 (9)	25.6 ± 1.2 (23)
27	182	8.94 ± 0.08 (25)	5.26 ± 0.27 (37)	0.26 ± 0.19 (25)	14.19 ± 4.79 (9)		31.77 ± 3.54 (9)	11.96 ± 1.30 (26)	0.01 ± 0.00 (10)	25.6 ± 1.3 (22)
28	154	6.53 ± 0.08 (23)	4.69 ± 0.36 (46)	0.41 ± 0.37 (23)	67.67 ± 26.16 (23)		0.10 ± 0.08 (22)	4.93 ± 0.19 (23)		22.6 ± 0.8 (23)
29	154	7.05 ± 0.11 (22)	4.74 ± 0.21 (42)	0.40 ± 0.36 (22)	59.00 ± 24.45 (22)		0.06 ± 0.04 (21)	4.92 ± 0.21 (22)		22.8 ± 0.9 (22)
30	154	7.99 ± 0.28 (24)	5.70 ± 0.49 (48)	0.53 ± 0.29 (24)	43.59 ± 16.32 (24)		0.08 ± 0.04 (23)	4.90 ± 0.19 (24)		22.9 ± 0.9 (24)
31	154	8.99 ± 0.07 (23)	5.98 ± 0.64 (44)	0.60 ± 0.30 (23)	38.42 ± 14.56 (23)		0.05 ± 0.03 (22)	4.92 ± 0.19 (23)		22.9 ± 0.8 (23)
32	210	6.59 ± 0.08 (29)	19.69 ± 2.72 (44)	0.39 ± 0.21 (29)	146.55 ± 60.67 (29)		0.10 ± 0.07 (29)	4.67 ± 0.16 (29)	0.05 ± 0.02 (29)	25.1 ± 0.5 (29)
33	210	7.09 ± 0.13 (29)	21.62 ± 2.81 (48)	0.47 ± 0.18 (29)	97.90 ± 57.07 (29)		0.07 ± 0.07 (26)	4.64 ± 0.14 (29)	0.05 ± 0.02 (29)	25.3 ± 0.5 (29)
34	210	8.07 ± 0.06 (29)	24.03 ± 0.71 (49)	0.44 ± 0.21 (29)	36.36 ± 10.63 (29)		0.08 ± 0.05 (29)	4.71 ± 0.20 (29)	0.04 ± 0.02 (29)	25.2 ± 0.4 (29)
35	210	8.96 ± 0.04 (29)	27.79 ± 3.33 (45)	0.52 ± 0.17 (29)	22.22 ± 7.67 (29)		0.22 ± 0.04 (28)	4.51 ± 0.29 (29)	0.05 ± 0.02 (29)	25.1 ± 0.4 (29)
36	152	6.54 ± 0.08 (20)	4.65 ± 0.36 (40)	0.09 ± 0.09 (20)	31.37 ± 7.32 (20)	0.58 ± 0.04 (19)	1.69 ± 0.20 (12)	4.80 ± 0.12 (20)		22.4 ± 0.7 (20)
37	152	7.00 ± 0.06 (20)	4.63 ± 0.27 (40)	0.10 ± 0.09 (20)	27.38 ± 6.57 (20)	0.57 ± 0.04 (19)	1.64 ± 0.22 (9)	4.79 ± 0.14 (20)		22.5 ± 0.6 (20)
38	152	8.05 ± 0.24 (21)	5.34 ± 0.18 (42)	0.11 ± 0.11 (21)	25.11 ± 5.79 (21)	0.57 ± 0.03 (20)	0.08 ± 0.05 (19)	4.78 ± 0.20 (21)		22.6 ± 0.5 (21)
39	152	8.97 ± 0.04 (19)	5.44 ± 0.22 (38)	0.27 ± 0.17 (19)	21.91 ± 3.73 (19)	0.56 ± 0.02 (18)	0.06 ± 0.04 (17)	4.75 ± 0.20 (19)		22.4 ± 0.5 (19)
40	199	6.48 ± 0.19 (29)	4.67 ± 0.28 (54)	0.42 ± 0.34 (29)	100.55 ± 51.60 (29)	10.06 ± 6.75 (28)	0.14 ± 0.08 (20)	4.90 ± 0.15 (29)		22.2 ± 0.6 (29)
41	199	7.03 ± 0.09 (29)	4.80 ± 0.29 (54)	0.40 ± 0.34 (29)	80.99 ± 44.49 (29)	9.53 ± 6.81 (28)	0.08 ± 0.04 (18)	4.91 ± 0.15 (29)		22.4 ± 0.6 (29)
42	199	7.98 ± 0.09 (29)	6.11 ± 0.57 (56)	0.37 ± 0.21 (29)	46.74 ± 18.95 (29)	4.74 ± 3.06 (28)	0.07 ± 0.05 (22)	4.94 ± 0.17 (29)		22.6 ± 0.6 (29)
43	199	8.98 ± 0.05 (29)	5.82 ± 0.48 (55)	0.54 ± 0.18 (29)	29.87 ± 9.64 (29)	2.43 ± 1.60 (28)	0.05 ± 0.04 (14)	4.85 ± 0.16 (29)		22.5 ± 0.6 (29)

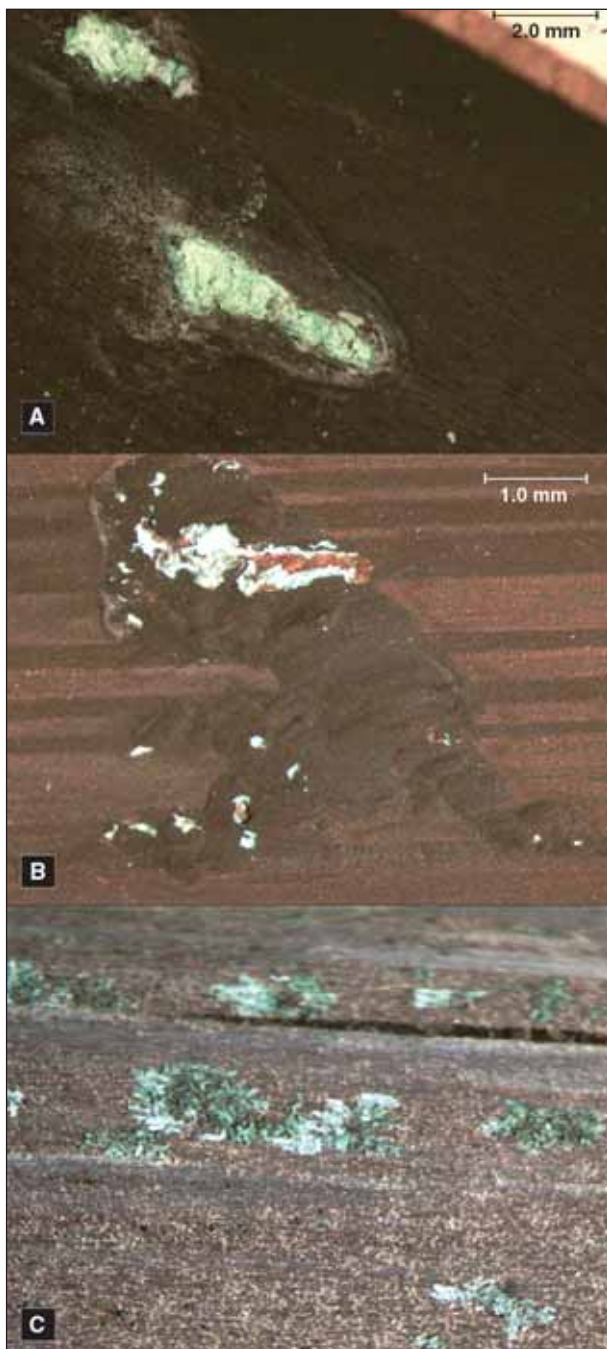
DIC—dissolved inorganic carbon

Blanks indicate that the parameter was not routinely measured in this run.

back to atmospheric pressure. The process was repeated, and the samples sat overnight to allow the resin to cure.

XRD. A theta–theta diffractometer⁹ with a copper X-ray tube was used to identify crystalline phases of the ground solids at USEPA’s Andrew W. Breidenbach Environmental Research Center in Cincinnati, Ohio. The tube was operated at 30 keV and 40 mA for most analyses. Scans

were typically performed over a 2-theta range from 5 to 60° with a step of 0.02° with a 3-s count time at each step. Pattern analysis was performed generally following ASTM procedures (ASTM, 1996) using a computer software program¹⁰ with reference to the 1995–2002 ICDD PDF-2 data files (International Center for Diffraction Data, Newtown Square, Pa).



Stereomicroscope images depict the corrosion by-product mounds that formed on the interior surfaces of copper pipes exposed to pH 9 water with 0 mg/L SO_4 in experimental run 9 (A), 5 mg/L SO_4 in run 10 (B), and 150 mg/L SO_4 in run 12 (C).

SEM and energy dispersive X-ray analysis (EDXA). SEM and EDXA were performed at USEPA in Cincinnati using an SEM microscope¹¹ and with attached EDXA analyzer.¹² Uncoated sample sections of small tubercles were mounted on 12-mm-diameter aluminum studs with double-sided carbon tape, and encapsulated pipe sections were mounted directly to the sample holder. The accelerating voltage was 15 keV, and an average count time of

180 s was used to obtain EDXA traces. The magnification used ranged from 100 to 3,000 \times .

RESULTS

Forty-three experimental runs were completed over several years to evaluate the effect of water chemistry on copper solubility and uniform and localized corrosion (Table 2).

Effect of sulfate and chloride. A series of experiments were conducted to evaluate the effect of sulfate (0, 5, 50 and 150 mg/L SO_4) on copper corrosion at pH 7, 8, and 9 in the presence of chloride (23–66 mg/L). Sulfate did not affect the appearance of the interior surfaces of copper pipes exposed to water at pH 7. Copper pipes were exposed to various sulfate concentrations during experimental runs 1–4 with conditions of low chlorine, 60–66 mg/L Cl^- , DIC of 10 mg/L C, and water temperature of 23°C. Light-green-colored solids were uniformly deposited across the surface of all pipes, independent of the sulfate level in the water. The shade and/or density of the solids appeared to vary slightly, with waters containing 5 and 150 mg/L SO_4 slightly darker in shade. No signs of localized pitting corrosion attack (e.g., mounds of corrosion by-products, irregular surface formations) were found under any sulfate condition.

Test runs 5–8 were conducted at pH 8 under conditions of low chlorine, 53–60 mg/L Cl^- , DIC of 10 to 11 mg/L C, and water temperature of 23°C. Copper pipes from these experiments appeared visually similar as a group (i.e., sulfate concentration did not affect appearance) but differed from pipes exposed to water at pH 7. The solids on the pipes were uniformly black with streaks of a light-green-colored solid over the entire surface. Visually, the level of sulfate did not change the pipe scale surfaces, and there was no indication of localized corrosion attack.

Runs 9–12 were conducted at pH 9 under conditions of low chlorine, 23–28 mg/L Cl^- , DIC of 10–11 mg/L C, and water temperature of 23°C. Copper pipes from these experiments were predominantly black in appearance. However, as shown in the photographs on page 122, all pipes had mounds of white and green to blue-green corrosion deposits. The mounds were randomly dispersed over the surfaces and present on the pipes under all test conditions. Notably, these corrosion by-product mounds also formed even when sulfate was absent from the water (stereomicroscope image A on page 122). In some cases, particularly with 50 mg/L SO_4 , the mounds appeared to be covered by the black solid, which was later identified as tenorite (image B on page 122). An apparent mix of white and green material was observed, particularly on pipes exposed to lower levels of sulfate, whereas the material appeared blue-green at the higher sulfate conditions. The mounds typically were oblong in shape, with the widest dimension in the direction of water flow. The longest dimension approached 10 mm or more in some cases. The corrosion mounds that formed in the 150-mg/L SO_4 water appeared to be more dispersed and were

not as well structured as under other water quality conditions (image C on page 122). Although the mounds of corrosion deposits observed at pH 9 and 10 mg/L DIC were similar in appearance to pit “caps” associated with localized corrosion, these observations alone were not enough to conclude that pitting corrosion was actively occurring in the pH 9 test waters.

To provide additional information, pipe sections from pH 9 experiments (test runs 9–12) were cut into smaller segments that were several inches long and solidified in an epoxy resin, as described previously. When hardened, the mounted pipe sections were cut with a diamond saw and polished to expose cross-sectional areas where corrosion by-product mounds were identified. Stereomicroscope images of the polished cross sections clearly showed that localized corrosion and pipe wall degradation was occurring below the corrosion deposit mounds (now appropriately referred to as pit caps). The two cross-sectional stereomicroscope images on page 123 show corroded copper below the pit cap. The thickness of the pit caps varied, with some pit caps as thick as a millimetre. In many cases, the pit cap appeared to extend into the pit itself. Pitting-attack penetration was as deep as 0.2 mm, or approximately 28% of the copper pipe wall. The pits were shaped like a bowl with the widest diameter at the cap–pit interface.

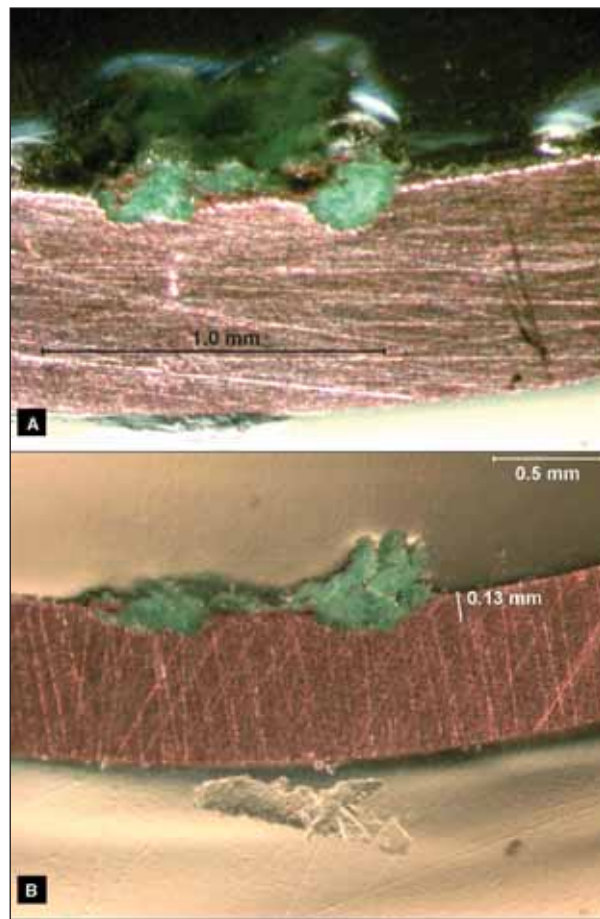
Pitting attack in copper pipes exposed to 0, 5, and 50 mg/L SO_4 appeared very similar in nature, whereas the extent of attack was less in pipes exposed to 150 mg/L SO_4 . Macroscale analysis of pipe cross sections clearly showed that localized attacks that were below the corrosion mounds had taken place after only 99 days. Had the experiments been carried out over a longer time period and had the pitting attack continued at a constant rate, penetration of the pipe wall and leaks would have begun in approximately 500 days.

To test the reproducibility of the previous observations, a series of test runs (36–39) was repeated in waters containing a slightly lower DIC (5 mg/L C), low chlorine, chloride only, and pH 6.5, 7, 8, and 9. Pitting corrosion of the copper pipe surfaces (as determined by the presence of corrosion by-product mounds and cross-sectional verification) was observed in water only at pH 9 (no sulfate and 25–37 mg/L Cl^-). The pipe surfaces appeared identical to those exposed to 10-mg/L C DIC water at pH 9 (image A on page 122).

SEM images from runs 9–11 uncovered more details about the nature of the localized corrosion attack and clearly revealed its extent. Distinct layers or zones of different solids were often seen within the pit or pit cap. In some cases, the pit was void of solids (particularly as sulfate concentration increased). Other instances showed signs of a developing membrane layer between the pit and the cap. As the amount of sulfate increased, distinct membrane layers became more apparent, and the separation between the material that made up the cap and the solid within the cap became more obvious. The composition of

the corrosion by-products associated with pitting attack changed with sulfate composition.

EDS elemental maps of pit cross sections showed that the composition of the corrosion by-products associated with localized corrosion changed with water chemistry. SEM and EDS scans showed the cross sections of pits formed in the absence of sulfate solids during experimental run 9. EDS analyses indicated that the cap material and solids within the pit contained copper, chloride, and oxygen. Pits on pipes exposed to 5 mg/L SO_4 contained predominantly copper, chloride, and oxygen, although small amounts of sulfur were noted at some locations (not shown). SEM and EDS scans also showed the cross section of a corrosion by-product mound from run 11. The pit caps associated with pits formed in water containing 50 mg/L SO_4 were predominantly composed of copper, sulfur, and oxygen. The material within the pit, however, was primarily composed of copper, chloride, and oxygen. There was visually less material in the pit relative to the pit cap, and many of the pits were void of material. These observations showed that as the sulfate concentration increased



In these stereomicroscope images, cross sections of corrosion by-product mounds show the degree of localized corrosion attack on the interior surfaces of copper pipes exposed to 0 mg/L SO_4 in experimental run 9 (A) and 5 mg/L SO_4 in run 10 (B), both at pH 9.

TABLE 3 X-ray diffraction results

Mineral	Chemical Formula	Color	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12
Cuprite	Cu ₂ O	Brown-red, purple-red, red-black	x	x	x	x	x	x	x	x	x	x	x	x
Tenorite	CuO	Black, steel gray			?		x	x	x	x	x	x	x	x
Malachite	Cu ₂ (CO ₃)(OH) ₂	Green, dark green, blackish green	x	x	x	x	x	x	x		x	x		
Nantokite	CuCl	Colorless, white, grayish, green									?	x		
Copper(II) hydroxy chloride*		Greenish black, dark green, green, yellow, black, blue-green, cyan					x	x	x	x	x	x	?	
Copper hydroxide sulfate hydrate	Cu ₄ (SO ₄)(OH) ₆ · 2(H ₂ O)	Blue-green												x
Brochantite	Cu ₄ (SO ₄)(OH) ₆	Green, emerald green, black										x	x	x
Langite	Cu ₄ (SO ₄)(OH) ₆ · 2(H ₂ O)	Blue-green, green-blue, sky blue										x		
Copper metal	Cu	Orange	x	x	x	x	x	x	x	x	x	x	x	x
Posnjakite	Cu ₄ (SO ₄)(OH) ₆ · (H ₂ O)	Blue								?		x	x	x

XRD—X-ray diffraction, x—mineral identified, ?—mineral possibly present

Blanks indicate mineral was not detected

*Copper(II) hydroxy chloride refers to a family of Cu²⁺ minerals with similar chemical composition. The minerals also have very similar XRD patterns, making it difficult to confidently identify the specific phase present. These minerals include calumetite [Cu(OH)Cl₂ · 2(H₂O)], atacamite [Cu₂Cl(OH)₃], paratacamite [Cu₂(OH)₃Cl], and eriochalcite [CuCl₂ · 2(H₂O)].

from 0 to 150 mg/L, the amount of sulfate in the pit cap increased. The material within the pit appeared to remain dominantly chloride-based and apparently was not affected by sulfate concentration of the water.

Presence of other mineralized solids. XRD analysis of copper pipe exposed to all experimental waters during test runs 1–12 identified the presence of cuprite and copper metal on the pipe surfaces (Table 3). In addition, solids formed on pipes exposed to pH 7 test waters (runs 1–4) all contained malachite. The presence of sulfate (5, 50, and 150 mg/L SO₄) did not change the mineralogical properties of the solids nor did the presence of sulfate (and chloride) promote the formation of copper sulfate (and copper chloride) crystalline phase mineral at pH 7. Solids formed on the surface of copper pipes exposed to water at pH 8 all contained tenorite (test runs 5–8). Malachite and one or more Cu(II)-chloride minerals (atacamite, paratacamite, calumetite, and/or eriochalcite) were identified on all pipes with the exception of the one exposed to the highest sulfate concentration (150 mg/L, test run 8), which contained neither. The presence of the Cu(II) sulfate mineral posnjakite was possibly present on pipes exposed to pH 8 water containing 150 mg/L SO₄. At least two different copper solids were present on the surface of copper pipes exposed to pH 9 waters. Tenorite was identified on all of the pipes (test runs 9–12). Malachite, Cu(II) hydroxy chloride minerals atacamite and paratacamite,

and the Cu(I) chloride mineral nantokite were all identified on pipes exposed to pH 9 water with 0 and 5 mg/L SO₄ (test runs 9 and 10). All pipes exposed to pH 9 waters that contained sulfate (test runs 10–12) had two or more Cu(II) sulfate minerals (langite, brochantite, and/or copper hydroxide sulfate hydrate) and lacked conclusive evidence of copper chloride minerals.

A few points and observations regarding mineralogical solids characterization should be noted. The XRD analysis reflected the bulk composition of all solids on the surface except for specific subsamples of pit or pit cap material. Therefore, mineral color identification (Table 3) must be considered when identifying specific features such as pit cap solids and uniform-scale solids. As shown by visual examination, the surface pipes that experienced localized attack, for example, were covered by a relatively uniform black solid whereas isolated areas of localized attack were covered by solids in a mix of blue and green shades. Tenorite was the only black solid identified by XRD, and all of the copper chloride and sulfate compounds were shades of blue and green. Second, the cupric sulfate and chloride minerals were absent at pH 7, and their abundance on the pipe surface increased with increasing pH and pitting tendency. Finally, cupric chloride and sulfate solids generally did not occur when malachite was the principal surface phase.

Effect of chlorine dose. Experimental runs were repeated, and new runs were performed to evaluate the effect that

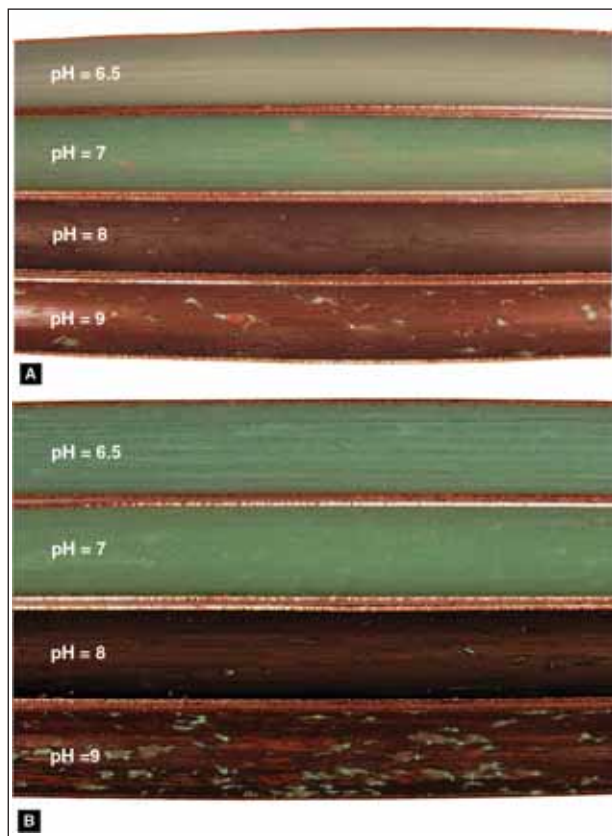
chlorine dose (added as NaClO in water over a pH range of 6.5 to 9 and DIC of 5 to 6 mg/L C) had on the development of localized corrosion. Results for pipes exposed to test waters with low free chlorine (test runs 40–43) agreed with findings of test runs 1, 5, and 9 with respect to the appearance of the surface and signs of localized corrosion (photograph A on page 125). Relatively uniform light-blue–green solids covered the pipe surface at pH 6.5 and 7, and no signs of localized corrosion attack were observed. Localized attack was apparent at pH 9 as shown by the presence of blue–green mounds of corrosion deposits and cross-sectional analysis of the pipe and mounds. A uniform light-black solid covered the pipe surface and local mounds in many cases. A uniform light-black solid covered the pipe surface exposed to pH 8 water as well, and close examination found a few, less-obvious local mounds. Cross-sectional analysis was not performed to verify whether pitting attack was in fact occurring in those areas. Pipe surface observations in the test waters with high chlorine concentrations (photograph B on page 125) were nearly identical to the low chlorine conditions, with the exception that there tended to be more uniformly deposited solids present and the presence of more corrosion deposits mounds at pH 9 and 8. Elevated chlorine doses appeared to enhance the rate of localized corrosion and expanded the range of pH values susceptible to pitting attack.

Regular addition of NaClO solution to maintain the free chlorine concentration in test systems did result in the buildup of high levels of chlorate from the stock solution in the test waters with time (Table 2). In general, the greatest chlorate levels were observed during lower pH test conditions because corrosion rates and chlorine demand were greater at lower pH. For example, average chlorate levels ranged from 2.4 to 10 mg/L during test runs 40–43 (Table 2), and chlorate levels ranged from 1.4 to 5.4 mg/L during test runs 1–12. Because the effect of chlorate ions on copper corrosion was not fully known, test runs 36–39 (DIC of 5 mg/L C and pH of 6.5 to 9) were repeated using a chlorine gas solution to adjust free chlorine levels in the tanks. Chlorate levels were independent of pH and averaged 0.6 mg/L (Table 2). The form of added chlorine (and chlorate ion) did not affect the appearance of copper pipe surfaces at any pH. At pH 9 (run 39), signs of localized corrosion were again evident in the blue–green mounds of randomly dispersed corrosion by-products among a relatively uniform layer of black corrosion deposits. The appearance was very similar to the case in which NaClO was used to adjust chlorine (run 43).

Effect of chloride and orthophosphate. For runs 13–16 and 21–24, recirculation experiments were repeated with chloride (15–38 mg/L) only (no sulfate) and 3 mg/L PO₄ at pH 6.5–9 and DIC of 5 and 10 mg/L C (Table 2). The surface of copper pipes exposed to orthophosphates in all water chemistries looked nearly similar but dra-

matically different from the cases in which orthophosphate was not present. There was a very thin, barely visible uniform layer of corrosion deposits on the pipes exposed to orthophosphates in any conditions. The pipes appeared new in that they were relatively shiny. There was no evidence of localized pitting corrosion attack (e.g., mounds of by-products, irregular surface formations) at any condition including pH 9 where pitting corrosion was clearly identified when phosphate was not present. XRD analysis identified only cuprite on the surfaces. It was also observed that orthophosphate at the dosed level (3 mg/L PO₄) greatly reduced chlorine demand, based on the frequency and amount needed to maintain the desired free chlorine residual. Orthophosphate appeared to significantly reduce the oxidation rate of Cu(I) to Cu(II), possibly by the formation of a thin amorphous cupric orthophosphate film. The exact nature or mechanism of the inhibition requires further study.

Effect of DIC. Recirculation experiments were conducted at pH 9 in water containing DIC of 28 mg/L C (run 35) and DIC of 50 mg/L C (run 20) to investigate the effect of DIC on localized corrosion (Table 2). As shown in photograph B on page 128, signs of localized corrosion were evident on pipes exposed to 25 mg/L C water,



The interior surfaces of pipes show the effects of exposure to waters containing low free chlorine levels in experimental runs 40–43 (A) and high chlorine levels in runs 28–31 (B) as a function of pH dose. Chlorine was added as sodium hypochlorite.

although the blue–green mounds of corrosion products were small in size relative to those observed in water with DIC of 5 mg/L C at pH 9 (photograph A, page 128). A spotty layer of tenorite was observed, and cuprite was identified on the surface of the pipes exposed to water with a DIC of 50 mg/L C (photograph C, page 128). No signs of pitting corrosion were observed. Increasing DIC increases the alkalinity and buffer capacity of the water and thus could play a role in preventing pitting corrosion.

Soluble copper levels. Soluble copper levels generally were lowest in conditions that favored pitting corrosion. For example, final copper concentrations were nearly 0.5 mg/L at pH 7 and < 0.05 mg/L at pH 9 in water containing 50 mg/L SO_4 and DIC of 10 mg/L C. These data demonstrated that localized copper corrosion did not translate to high copper levels.

DISCUSSION

Implications for other studies and experimental systems. This research demonstrated that localized or pitting corrosion can be studied at the pilot scale in reasonable time frames (e.g., several months). Study time frames were on the same order as periods needed for the study of uniform corrosion and metal solubility–related work, and studies can be performed in waters having representative drinking water chemistries without the addition of stimulating variables outside the range that might be expected in real drinking waters.

This research provided evidence to suggest that water utilities can construct relatively simple copper pipe–rig pilot systems to investigate their water’s tendency to induce pitting, predict the effect of water treatment or water quality changes on pitting tendency, and study approaches to reduce pitting tendencies. For example, copper pipe loops located at the treatment plant or in the distribution system and operated in a single-pass continuous-flow-through mode at the appropriate flow rate could provide useful information at minimal cost and effort. Periodically observing the interior pipe surface of such a system would provide visual indications of localized corrosion attack and possibly lead to a better understanding of pitting corrosion. Furthermore, the findings described here suggest that experimental systems can be set up to systematically examine the effect of types of water quality variables and corrosion inhibitors on pitting corrosion. Such work is currently being conducted in conjunction with several water utilities. Additional work is needed to further evaluate the practical usefulness of such systems.

Conditions associated with pitting corrosion. These findings showed that waters with a certain combination of pH, chloride, and DIC conditions are associated with the initiation and continued propagation of pitting corrosion, within the time periods studied. Specifically, high pH (pH 9 and possibly as low as 8), low DIC (< 10 mg/L

C and possibly as high as 25 mg/L C), and chloride levels of 14 to 38 mg/L promoted pitting corrosion. The way in which free chlorine was maintained (chlorine gas solution or NaClO) did not appear to affect the extent of pitting corrosion attack. Visual observations suggested that elevated free chlorine levels enhanced the rate of localized corrosion and expanded the range of pH values susceptible to pitting attack.

The presence of sulfate was not necessary to induce and propagate pitting corrosion. These experiments did not answer the question of whether sulfate in the absence of chloride could produce pitting corrosion. Sulfate did affect the composition of the pit cap; Cu(II) sulfate minerals displaced Cu(II) chloride minerals as sulfate concentration in the water increased. Sulfate did not appear in the pit itself where active localized attack of copper metal occurred. Only chloride was in contact with the copper surface at the point of metal degradation (anode), suggesting that its presence is essential to pit propagation. Sulfate at 150 mg/L appeared to decrease the severity of localized corrosion attack. This work documented a relatively narrow range of water variables that support pitting attack. Additional research must be performed to obtain a better understanding of the relative importance of these key parameters and at what minimum values these key parameters become problematic.

Possible mitigation strategies and associated risks. This research also showed that the initiation of pitting corrosion observed in some high-pH and low-DIC waters can possibly be prevented, but the mitigation strategies must be selected with considerable caution. For example, increasing DIC to 49 mg/L C prevented the initiation of pitting corrosion at pH 9. However, such high-DIC concentrations risk considerably elevated soluble copper release (particularly in new plumbing), and the copper action level could be exceeded (Schock et al, 1995). In fact, soluble copper levels increased quickly in the recirculation experiments until the solution became supersaturated with cupric hydroxide and deposition throughout the experimental system began occurring. Within several weeks, the precipitation evolved into a quasi-equilibrium state of copper release from the pipe, balanced by malachite deposition in the bulk water. That deposition in the tanks, however, did not form a protective deposit on the copper pipe surfaces.

The addition of 3 mg/L PO_4 orthophosphate (added as a nonzinc-containing chemical) to pH 9 and low-DIC water prevented pitting attack when chloride ranged from 15.4 to 36.6 mg/L Cl^- , but the resulting soluble copper levels exceeded those obtained without orthophosphate at DIC levels of 10 and 25 mg/L C. Preliminary in-house research and field observations (Lytle, 2006) have suggested that polyphosphates may be even more effective than orthophosphate at preventing the initiation of copper-pitting corrosion in water, but they risk elevating lead and copper release in some waters. Considerably more

research is necessary to fully understand the role of phosphates in preventing pitting corrosion.

The observations made in this work appear to be in agreement with some real-world pinhole leak cases (Table 1). Relatively high-pH waters having low DIC and containing significant levels of chloride and sulfate are associated with localized corrosion. Given the controlled nature of this work and similarities in water quality (pH, DIC, sulfate, and chloride), it is reasonable to assume that the cause of pinhole leaks experienced by communities presented in Table 1 was simply a favorable combination of pH, DIC, and chloride in their finished waters. Factors such as aluminum, silica, total organic carbon, bacteria, and other variables often implicated as the source of pitting attack are not necessary to initiate pitting corrosion in the field cases. Though this work showed they are not necessarily prerequisites to propagate pitting, factors such as these may either accelerate or decrease localized corrosion.

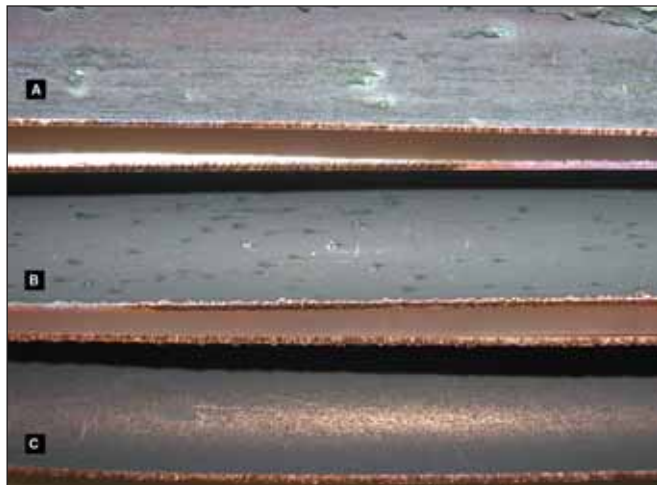
Pitting mechanisms. The mechanism(s) for pit initiation in high pH and low DIC water containing chloride and sulfate remains speculative at this point, and further research is needed. However, the observations and water chemistry in this work suggest that some fundamentals of a reasonable mechanism consistent with solution chemistry theory and experimental observations can be proposed. Low inorganic carbon is probably important for several reasons. Perhaps most significant is the buffering capacity or intensity of most waters, which is predominantly controlled by the combination of DIC and pH unless the concentration of other weak acids (such as phosphoric) are high, relative to the carbonate content. At any given pH, waters containing lower DIC are more poorly buffered. The buffer intensity curve is complex in shape, and a local buffer capacity minimum occurs at a relatively high pH of approximately 8.3 (Stumm & Morgan, 1996). As a result, local pH differences between cathodes and anodes on the copper pipe surface can reasonably be assumed to be greatest in water with relatively high pH and low DIC. Such differences could favor the establishment of a localized corrosion cell.

Cathodic reactions cause an increase in pH, resulting from the reduction of oxygen or oxidizing agents (such as disinfectants) in water, and the extent of changes in pH is dependent on water quality and reaction time. The increased pH in the region attracts cations and creates a local environment conducive to the precipitation of certain solids, depending on background water composition. Because aluminum, calcium, iron silica, and other common drinking water constituents were not present in the test waters, only copper solids should be considered. Copper metal is oxidized at the anode, and positively charged copper ions are released from the corroding pipe wall. The hydrolysis of copper ions leads to a local drop in pH in

the region. The copper ion speciation in the region changes as well, to a mixture of cationic, anionic, and nonionic species because of chemical complexation (primarily hydroxide, bicarbonate, carbonate, and mixed complexes). The lower the pH, the more positively charged are the copper aqueous species that form. Anions including chloride and sulfate will diffuse to the anode where electroneutrality must be maintained. Chemistry at the anode may also favor the precipitation of solids, the nature of which could differ from the cathode depending on the magnitude of pH difference, anions present, and the pH stability region of the solid. For example, the buildup of Cu^{+1} and/or Cu^{+2} and Cl^- at the anode could favor the localized deposition of copper chloride compounds such as those identified in this work. Similarly, such solids could form under high pH conditions at the cathode. Such examples underscore the importance of thermodynamic considerations in the development of models to explain the nature of pitting corrosion.

The precipitation of solids at an anode or cathode leading to the initiation of pitting corrosion has been considered by other researchers (Marshall & Edwards, 2005; Page et al, 1974). The deposited solid can be a barrier against oxidant diffusion to the copper surface, and an oxidant gradient is then established between neighboring regions. The anode is located in the oxygen-limited region below the solid, and the cathode is free to interact with high oxygen (or disinfectant). In the current research, however, water chemistry was tightly controlled and only copper compounds—namely hydroxy chloride and hydroxy sulfate—were associated with the pitting regions. The identification of copper chloride and sulfate compounds only when pitting was identified suggests that they are intimately involved with the pitting process. Other researchers drew similar conclusions about the presence of brochantite in pitting in hot water systems after observing that it appeared in pit caps (Edwards et al, 1994a).

The role of orthophosphate can be reasonably explained within the context of the previous discussion. Orthophosphate will exist in a charged anionic form and be preferentially attracted to the anode because of its greater negative charge relative to chloride (and sulfate). Because of this preferential attraction, phosphate ions displace chloride as well as sulfate from the region. Orthophosphate reduces the solubility of copper by producing a relatively insoluble copper phosphate compound over a very broad pH range (Schock et al, 1995). Therefore the precipitation of copper would be relatively uniform because a similar material would cover both the anode and cathode. DIC might reduce the initiation of pitting by limiting the pH difference between local corrosion cells and the likelihood for nonuniform deposition of solids. Second, phosphate is attracted to the anode and may repel chloride ions. And third, carbon-



Localized corrosion is evident on the interior surfaces of copper pipes exposed to pH 9 waters with dissolved inorganic carbon of 5 mg/L C (A), 25 mg/L C in run 35 (B), and 50 mg/L C in run 20 (C).

ates form strong aqueous complexes with Cu^{+2} and therefore increase its solubility. Increasing the solubility of copper might decrease the tendency to precipitate the specific compounds at the electrodes that lead to pitting corrosion.

The intent of this discussion has been to suggest possible mechanisms and stimulate thoughts about factors or combinations of factors needed to initiate pitting corrosion. Obviously, these ideas are unproven, and the topic remains of major importance to drinking water consumers and highly worthy of future research.

CONCLUSIONS

The findings of this work showed that pitting corrosion of copper plumbing was favored in waters with low chlorine concentration and DIC (5 and 10 mg/L C and possibly at 25 mg/L C) and in high-pH water (pH 9) in the presence of chloride. Pitting corrosion was not observed at pH 6.5 and 7 and was evident at pH 8 only when higher chlorine levels were maintained. Although sulfate was not necessary to develop pitting corrosion, it did affect the composition of the corrosion by-products associated with pitting corrosion. Only chloride was in contact with the copper metal surface at the point of degradation (anode), suggesting the ion's presence was necessary for pit propagation. Increasing the DIC to 50 mg/L C or adding orthophosphate at 3 mg/L PO_4 prevented the initiation of pitting corrosion at pH 9.

As these research findings point out, copper-pitting corrosion fundamentally can occur in water with a favorable combination of chloride, pH, and DIC (and possibly sulfate). More communities are experiencing widespread pinhole leak incidents and also have water with the qualities that fall within the favorable bounds roughly defined in this work. In such real cases, however, factors including silica, aluminum, sulfides (sulfate-reducing bacteria),

organic carbon, and other water quality variables are often (and perhaps incorrectly) suspected as the cause of the problem. Finally, the work demonstrated that localized or pitting corrosion can be studied at the pilot scale in reasonable time frames (e.g., several months) using a simply designed system.

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FOOTNOTES

- ¹Whatman, Hillsboro, Ore. or Ricca Chemical Co., Arlington, Texas
- ²Model DO175, Hach Co., Loveland, Colo.
- ³Model 50180, Hach Co., Loveland, Colo.
- ⁴Model 61E® Thermo Jarrel Ash, Franklin, Mass.
- ⁵Model 5011, UIC, Joliet, Ill.
- ⁶Model 50, UIC, Joliet, Ill.
- ⁷Conrad 70TM, Decon Labs Inc., King of Prussia, Pa.
- ⁸EpoThin™, Buehler Ltd., Lake Bluff, Ill., or equivalent
- ⁹XDS-2000, Scintag Inc., Santa Clara, Calif.
- ¹⁰Jade, Versions 5-7, Materials Data Inc., Livermore, Calif.
- ¹¹Model 5300, JEOL Ltd., Peabody, Mass.
- ¹²Link Analytical Inc., Madison, Wis.

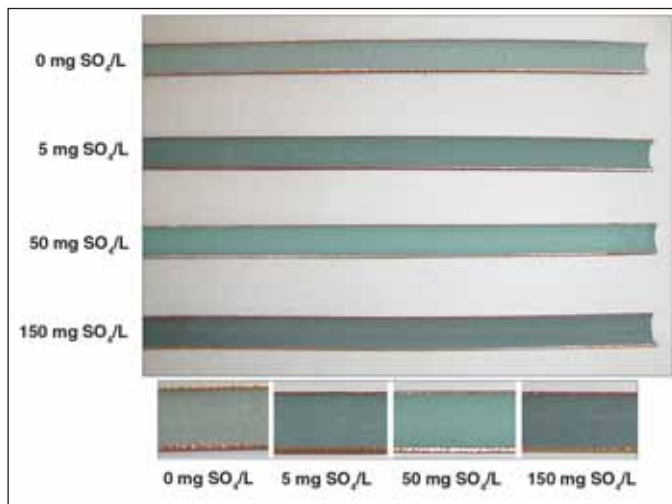
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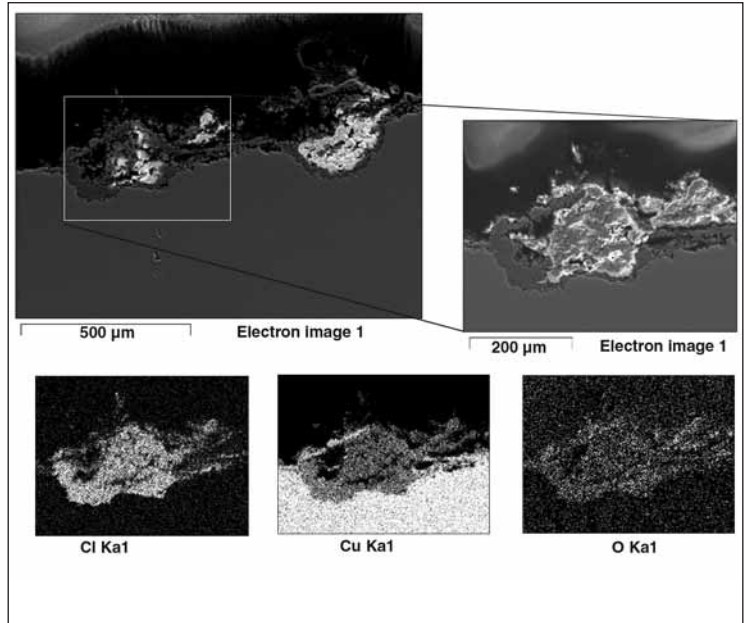
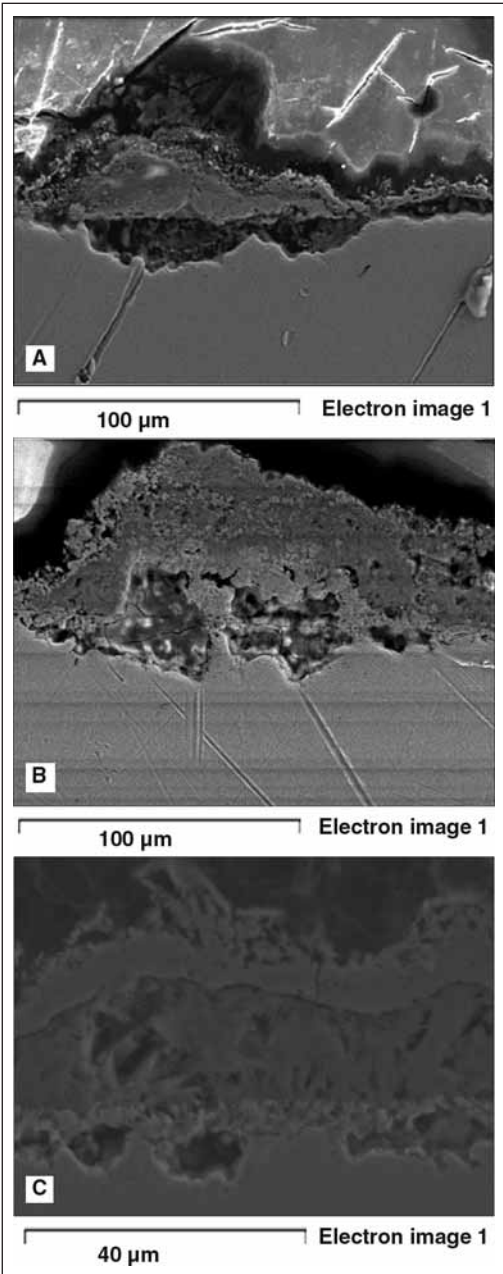
The pilot-scale copper recirculation system used in these experiments included 200-L (53-gal) heavy-duty polyethylene tanks.



Photographs from runs 1–4 offer a side-by-side comparison (top) and close-up views (bottom) of the interior surfaces of copper pipes exposed to 0, 5, 50, and 150 mg/L SO_4 at pH 7. Uniform deposits of light-green-colored solids are evident across the surfaces of all pipes.

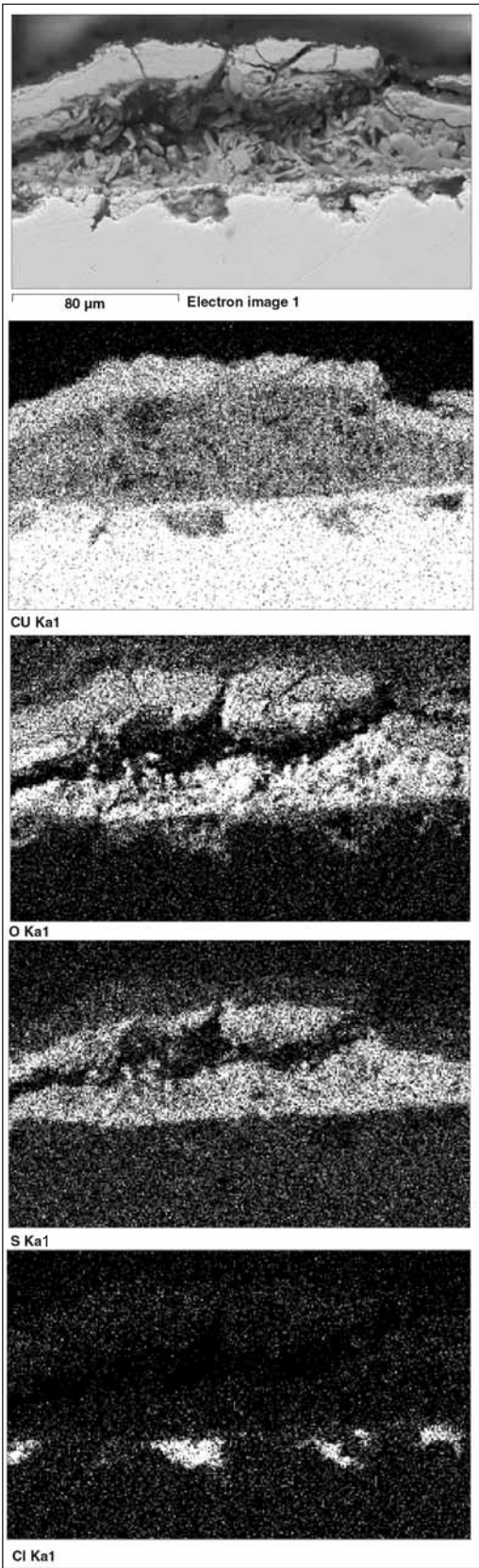


The interior surfaces of copper pipes exposed to 0, 5, 50, and 150 mg/L SO_4 at pH 9 (experimental runs 9–12) show pipe surface scales. A close-up image highlights the randomly dispersed blue-green corrosion by-product.

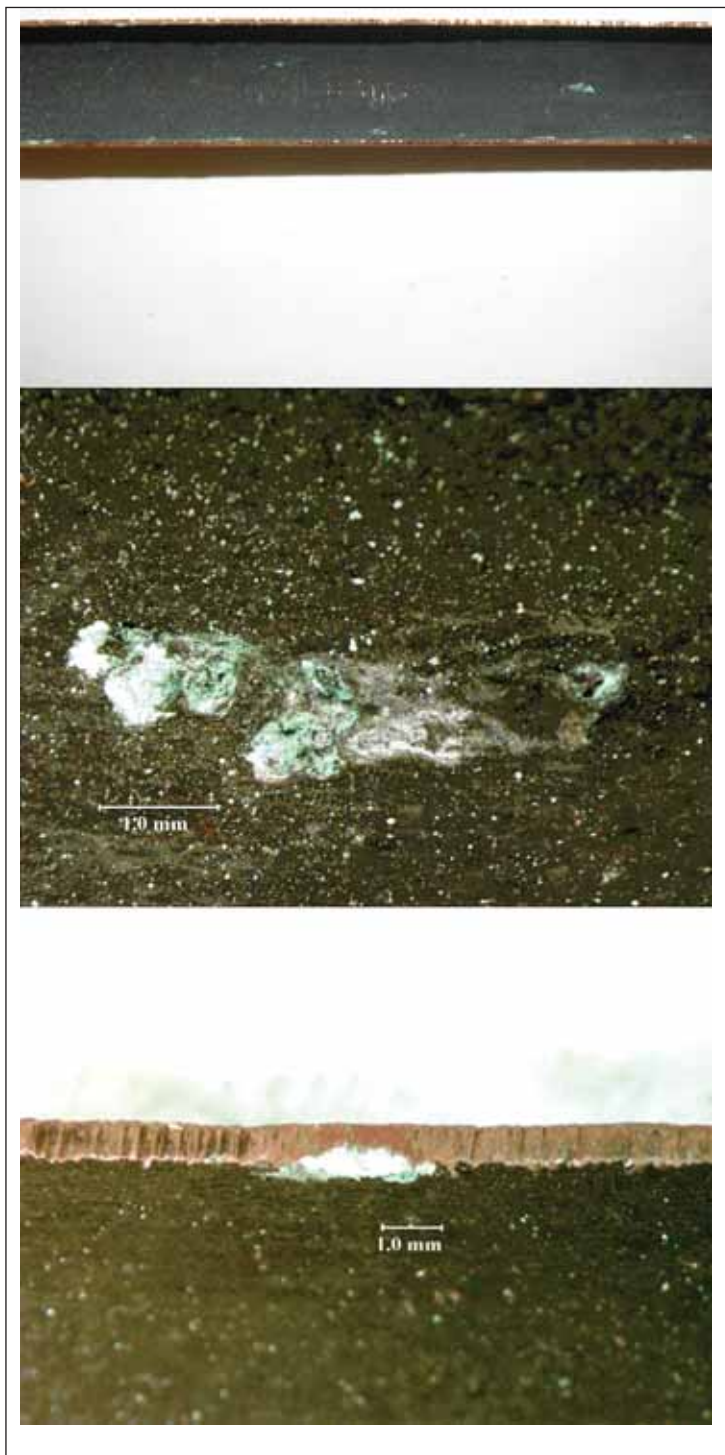


Scanning electron micrograph and energy dispersive spectroscopy elemental scans show the cross section of a corrosion by-product mound formed in the absence of sulfate on the interior surfaces of copper pipes (exposed to 0 mg/L SO_4 at pH 9 during experimental run 9).

Scanning electron micrographs depict the cross sections of corrosion by-product mounds and degree of localized corrosion attack on the interior surfaces of copper pipes exposed to pH 9 water with 0 mg/L SO_4 in experimental run 9 (A), 5 mg/L SO_4 in run 10 (B), and 50 mg/L SO_4 in run 11 (C).



Cross sections of a corrosion by-product mound formed on the interior surfaces of copper pipes exposed to 50 mg SO₄ at pH 9 (experimental run 11) are shown in these scanning electron micrograph and energy dispersive spectroscopy elemental scans.



Photographs and stereomicrographs show the interior of copper pipes exposed to pH 9 water (run 39) with the free chlorine residual adjusted with chlorine gas.



During experimental runs 14-16, the interior surfaces of copper pipes were exposed to 2.9 to 3 mg/L orthophosphate at different pH values and dissolved inorganic carbon of 10 mg/L. A thin, barely visible uniform layer of corrosion deposits was seen on pipes exposed to orthophosphates in any conditions.