

The Effect of Phosphate on the Properties of Copper Drinking Water Pipes Experiencing Localized Corrosion

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Abstract Extensive localized or pitting corrosion of copper pipes used in household drinking water plumbing can eventually lead to pinhole water leaks that may result in water damage, mold growth, and costly repairs. Water chemistry has been recognized as the cause of some community-wide copper pinhole leak outbreaks. A large drinking water system in Florida recently switched from pH adjustment and orthophosphate addition to a blended orthopolyphosphate chemical to address this problem. The objective of this study was to examine the impact of phosphates on the morphology and elemental composition of the interior surface of failed copper pipes removed from homes in the community. Scanning electron microscopy (SEM) and energy dispersive spectroscopy analysis of pipe surfaces revealed the build-up of phosphorus over time. Phosphorus was most greatly concentrated over areas of localized corrosion attack. Examination of the corrosion by-product mounds that covered corroding pits showed that phosphorus had migrated to the region adjacent to the copper pipe wall. Distinct copper–phosphorus solids were identified under SEM magnification; however, no crystalline copper–phosphate compound was identified by x-ray diffraction analysis.

Keywords Copper · Pitting corrosion · Phosphate · Drinking water

Introduction

Copper is widely used in home plumbing and distribution system piping material. Although copper is relatively resistant to corrosion, it is not inert and can experience both uniform and non-uniform corrosion in water under certain conditions. Uniform corrosion describes the corrosion of a metal evenly across the surface which often leads to the relatively uniform deposition of corrosion by-products over the pipe surface, while local corrosion results in concentrated areas of corrosion attack. These localized areas of corrosion in copper pipes, also known as “pitting” corrosion, can be a major cause of premise plumbing failure. In relatively short periods of time after copper plumbing installation, copper pitting can occur, and eventually 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. Additionally, pinhole leaks may go undetected in walls or basements for months, providing an environment conducive to mildew and mold growth.

Pitting corrosion of copper plumbing materials in water is complex and not well understood despite a number of studies on the topic [1–7]. Pit initiation has been associated with many factors including microbial activity, copper material imperfections, excess carbonaceous manufacturing residues on the pipe surface, water chemistry, stray currents, soldering flux, and other variables within a given distribution system. A number of water chemistry parameters including pH, alkalinity, dissolved inorganic carbon (DIC), chloride, organic carbon, aluminum, chloramines,

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sulfide, and sulfate have been associated with the initiation and propagation of pitting corrosion.

Pitting corrosion of copper in water has been categorized into at least three types based on water chemistry and physical features: cold-water (Type I) [2, 8–10], hot-water (Type II) [11], and soft-water (Type III) [12]. Soft-water copper pits are described as being relatively wide and shallow and consisting of an exterior layer of bronchantite [$\text{Cu}_4(\text{SO}_4)(\text{OH})_6$] and/or malachite [$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$] over a layer of crystalline red-brown cuprite [Cu_2O] and the corroding copper surface. The voluminous corrosion deposits of the exterior layer are released to the water and can potentially cause water blockage. Waters having low conductivity, low alkalinity, and relatively high pH are typically associated with soft-water pitting.

While the role of orthophosphate on lead corrosion and solubility are fairly well understood [13–16], the role of phosphates on copper pitting corrosion has not received much attention. From these few investigations, it has been shown that phosphates (orthophosphates and/or polyphosphates) are effective at preventing copper pitting corrosion problems in some situations. Lytle and Schock [17], for instance, reported that 3 mg PO_4/L orthophosphate prevented localized corrosion attack of copper pipes in low DIC, high pH, and high chloride water. Tests were conducted using pilot-scale recirculating copper pipe loops, and results were based on surface analysis of internal pipe wall surfaces. Also, while investigating a case study of pitting corrosion in southwest Ohio, Lytle and Nadagouda [18–20] observed that neighboring communities using the same source water did not report pitting corrosion cases. Upon close investigation, it was found that the neighboring communities applied polyphosphates to their finished water for corrosion control or prevention of calcium precipitation.

The majority of research on the role of phosphates on copper corrosion and solubility, however, is based on relatively short-term electrochemical studies. The representativeness of these approaches to actual drinking water distribution system conditions is questionable. Past efforts have also focused on new copper surfaces, and subsequent conclusions apply to the prevention of pitting rather than stopping well-established cases of in situ pitting attack. There are no conclusive data to support the benefit (and associated mechanisms) of phosphates on aged copper pipes that have experienced years of localized corrosion attack. Furthermore, there are no reports on how phosphates impact corrosion by-products and solids associated with localized corrosion found on old copper plumbing.

Therefore, the objective of this work was to investigate the morphological features and elemental composition of corrosion by-products and solids associated with pitted copper pipes before and after blended ortho-polyphosphate treatment. In order to assess the effectiveness of past and current treatment strategies, including the impact of

phosphates on pitting corrosion, affected pipes needed to be removed and analyzed. Systematic removal, examination, and comparison of the surface of copper pipe specimens subjected to varying times into corrosion control treatment with phosphate inhibitors was conducted from a distribution system suffering from wide-spread pitting corrosion of copper piping. Pipe comparisons were based on a number of solids surface analysis approaches including x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray analysis (EDXA). It is important to state that this work was not intended to identify the specific cause of pitting corrosion or determine whether phosphate treatment was effective in reducing pinhole leaks in this case study. Rather, the purpose was to report on the physical features of areas of local corrosion attack before and after the implementation of a phosphate-based corrosion control program.

Background

A water distribution system in Florida supplies approximately 210,000 customers. Historically, the test utility was supplied with water from a neighboring utility to the north. The neighboring utility's water is a mixture of surface water from a lake and groundwater, and is treated by physical and chemical processes. The neighboring utility has added a zinc polyphosphate for corrosion control at a target dosage of 1.2 mg total PO_4/L (0.1 mg Zn/L) for years. In 1995 and 2002, the test utility added its own water sources to the supply from the neighboring utility. As of 2006, the test utility's distribution system was supplied by the neighboring utility's water in the north (40% of total supply) and a blend of test utility treated water (30% of total supply) and water from a local river (25% of total supply) in the southern service area. A mixing zone of these waters exists between the north and south. The test utility treats groundwater using electro dialysis reversal and other physical/chemical processes.

The test utility's distribution has been experiencing a wide-spread and publicly visible outbreak of pinhole leaks in household copper plumbing. The first pinhole leak problem was documented in 1998 and hundreds have been reported since. In an attempt to mitigate the problem, the utility switched from pH adjustment to orthophosphate addition as their corrosion control strategy in 2003. The target pH was also decreased from 8.4 to 7.5. Orthophosphate was initially added at 3 mg PO_4/L and was then decreased to 1 mg PO_4/L 6 months later. The decision to switch to orthophosphate was prompted by the success of orthophosphate in reducing copper pinhole outbreaks in other distribution systems [21]. However, the number of household copper pitting episodes continued to increase in

the system. In September 2005, the utility decided to change their chemical formulation to a 50:50 ortho-poly-phosphate blend, which was the treatment strategy at the time of manuscript preparation. As part of the new corrosion control program, distribution system water samples were analyzed for a wide range of water quality parameters to assess the distribution of phosphorus into the distribution system.

In conjunction with the utility’s effort, this study systematically examined and compared the surface of copper pipes removed from residences in the utility’s service area at different time periods into corrosion control treatment with phosphate inhibitors. It was anticipated that by examining the interior surface of copper pipes removed from the distribution system in a progressive temporal manner that assessment on the effectiveness of past and current treatment strategies would help to provide insight into mechanism(s) of phosphates in reducing established copper pitting corrosion.

Failure Analysis

Experimental System Design and Operation

Copper pipe sections from homes within the southern section of the utility’s distribution system were collected at various stages of phosphate treatment. Pipe sections were shipped dry with appropriate chain of custody documentation to the USEPA’s Andrew W. Breidenbach Environmental Research Center (AWBERC) (Cincinnati, OH, USA). Pipe removal date, pipe age, and the location of the home from which the pipe was removed were provided. Upon receipt, pipe specimens were logged, photographed, and given identification numbers.

Distribution system water quality sampling was performed on a monthly basis beginning in March 2006, at 15 sites in the distribution system. The sites were evenly distributed into three zones (north, south, and mixing zones) to ascertain the effectiveness of the phosphate feed, and to provide a general understanding of water chemistry throughout the system. Samples were analyzed for free and total chlorine, oxidation–reduction potential (ORP), and temperature in the field, and iron, calcium, magnesium, manganese, zinc, alkalinity, ortho- and total-phosphate, chloride, nitrate, and ammonia at the USEPA laboratory. The results of the study are summarized in Table 1.

Analytical Methods

The pH was measured with a Hach Company (Loveland, CO, USA) EC40 bench-top pH/ISE meter (Model 50125). The instrument was standardized daily using a two-point

Table 1 County distribution system water quality analysis summary

Zone	pH ^a	Free Cl ₂ (mg/L) ^a	Total Cl ₂ (mg/L) ^a	Temperature (°C) ^a	Conductivity ^a	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	NH ₃ (mg N/L)	NO ₂ (mg N/L)	NO ₃ (mg N/L)	Total phosphate (mg PO ₄ /L)	Orthophosphate (mg-PO ₄ /L)	SiO ₂ (mg/L)	SO ₄ (mg/L)	Total alkalinity (mg CaCO ₃ /L)	Zn (mg/L)
South Zone	7.40	0.29	3.18	25.3	753	49	4.0	23	61	1.05	0.10	0.56	1.60	0.95	16.3	199	44	0.004
Mixing Zone	7.57	0.33	4.27	25.8	714	40	4.0	22	56	1.39	0.00	0.41	1.70	1.00	7.0	194	48	0.006
North Zone	7.53	0.29	3.34	26.1	577	54	5.2	19	28	1.10	0.00	0.26	1.02	0.32	10.0	179	57	0.033

Values represent average of five different locations sampled monthly between 3/28/2006 and 2/26/2007

^a Measured in the field

calibration with pH 7 and 10 standard solutions (Whatman, Hillsboro, OR, USA). ORP was measured with a Corning pH/ion meter 450 (Corning Incorporated, Corning, NY, USA) with two Orion[®] combination redox electrodes (Orion Research, Inc., Beverly, MA, USA). Total phosphorus, silicon, calcium, sulfur (sulfate), and copper were measured with a Thermo Jarrel Ash (Franklin, MA, USA) 61E[®] purged inductively coupled argon plasma spectrometer (ICAPS). Chloride was analyzed using an automated potentiometric titration approach (Standard Methods 4500-Cl-D) [22]. Free and total chlorine was analyzed according to the Hach DPD colorimetric method [22]. DIC was analyzed by a coulometric procedure on a UIC Model 5011 CO₂ coulometer (Joliet, IL, USA) with Model 50 acidification module, operated under computer control, equivalent to ASTM D513-02 Method (B). Enhancements in sample gas stripping and sample handling were implemented to improve analytical speed and accuracy.

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 special interest, were photographed (3× magnification). A stereomicroscope with digital camera was used to capture magnified images (20× magnification) of the areas of interest. The pipe section was then placed on aluminum foil and in an oven set at 150°F ± 10°F for 15 min. Several grams of epoxy resin (Buehler EpoThin[®] or equivalent) were prepared, and the resin was lightly dabbed onto defects or areas of localized corrosion. The sample was wicked from the resin into the defects to reduce porosity in the mounted section. The pipes were then placed into a vacuum chamber with the defects facing up and a vacuum of at least 23 inches of mercury was pulled for 2 min. The vacuum was released to allow the samples to come back to atmospheric pressure. The process was repeated and the samples set overnight to allow the resin to cure.

X-ray Diffraction

A Scintag (Scintag, Inc., Santa Clara, CA, USA) XDS-2000 theta–theta diffractometer with a copper x-ray tube was used to identify crystalline phases of the ground solids. The tube was operated at 30 keV and 40 mA for most analyses. Scans were typically performed over a 2-theta range between 5° and 60° with a step of 0.02° with a 3-second count time at each step. Pattern analysis was performed generally following ASTM procedures (ASTM 1996) using the computer software Jade (Versions 5-7, Materials Data, Inc.) with reference to the 1995–2002

ICDD PDF-2 data files (International Center for Diffraction Data, Newtown Square, PA, USA).

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis

Nearly all SEM images and EDXA were obtained using a JEOL 5800 scanning electron microscope (SEM) (Peabody, MA, USA) with an attached Oxford Analytical (EDXA) (Madison, WI, USA). Uncoated samples of pit caps and pipe sections 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 20 keV, and an average count time of 180 s was used to obtain EDXA traces. The magnification used ranged from 100× to 3000×, and EDXA results were reported as weight% unless otherwise noted. Oxygen was calculated by stoichiometry and all results were normalized to 100%. Prior to elemental analysis, the EDXA system was optimized, according to manufacturer's protocol, using an uncoated copper grid. It should be noted that although quantitative analysis is implied by the instrument manufacturer, the authors did not perform additional standardization steps and consider EDXA data to semi-quantitative in nature. As such, EDXA results should be interpreted accordingly.

Results

Pre-treatment Assessment

The exterior surfaces of failed copper pipe sections removed from residences located in the southern and blended water zones (Fig. S1) show the extent of damage caused by pitting corrosion. The blended water zone receives a significant fraction of water from the neighboring utility. The neighboring utility's water (and water in this blended zone) is considered "less aggressive" due to much fewer reported cases of pinhole leaks. However, the fact remains that pinhole leaks still occurred in both the blended zone and the southern region. Holes in the walls of failed pipes are as large as 2.2 mm in diameter, and pipe failures typically occur beneath the concrete slab foundations of homes without basements. Leaks were often identified by the homeowner after the sound of running water was detected when no faucets or valves were open, or after water had worked through cracks in the concrete slab. Homes built on concrete slabs (without basements) are common practice in the region, and explains why leaks were typically not detected when the pipe wall is initially breached, but rather after holes had grown to much larger diameters. There is no certain way to know how much time

passed between the establishment of the initial pinhole leak and the leak's detection, which also complicates assessment of the problem.

A number of failed copper pipe sections from the test utility's distribution system have been examined by USEPA investigators over the past several years. The following discussion will focus on a detailed examination of the interior surface of copper pipe sections removed from four different residences located in the southern zone of the distribution system. Most importantly, the pipes were removed at different times into phosphate treatment. The specific pipes examined in this study were removed: (1) 1 year after the start of orthophosphate addition (prior to blended phosphate addition), (2) 1 month after the start of blended phosphate addition (orthophosphate was added for the previous 2 years), (3) 9 months after the start of blended phosphate addition (orthophosphate was added for the previous 2 years), and (4) 1 year after the start of blended phosphate addition (orthophosphate was added for the previous 2 years). Comparisons of the pipe surface properties will help system operators assess the impact of phosphates on localized pitting corrosion attack and understand mechanism(s) of action on pipe.

One Year After Orthophosphate Addition

The interior base surface of the copper pipe section removed 1 year into orthophosphate treatment (sample ID dl00255) was dark orange in color. A large streak of white to cream-colored and various shades of green and blue solids were deposited on half of the pipe below where a pinhole leak had developed (Fig. 1a). There were also a number of randomly deposited dark green mounds of solids of various sizes, many of which were covered with a cream-colored deposit layer. Stereomicroscopic examination of the local deposits showed the extent to which the cream-colored material covered and surrounded the dark green (presumably copper corrosion by-product) mounds (Fig. S2a). Removal of a green mound revealed a light orange-colored and porous surface (Fig. S2b). The solid resembled the porous membrane typically associated with localized corrosion attack that separates the pit cap from the pit [1]. The presence of corrosion by-product mounds and a porous membrane does not necessarily indicate a location of pitting corrosion attack. Examination of the cross section of the corrosion mounds, however, confirmed that pitting corrosion was taking place in these areas (Fig. S2c). The cross section clearly shows the features commonly associated with pitting corrosion: pit cap, porous membrane, and pit.

EDXA analysis of the copper pipe section surface showed that silicon, copper, and oxygen covered nearly the

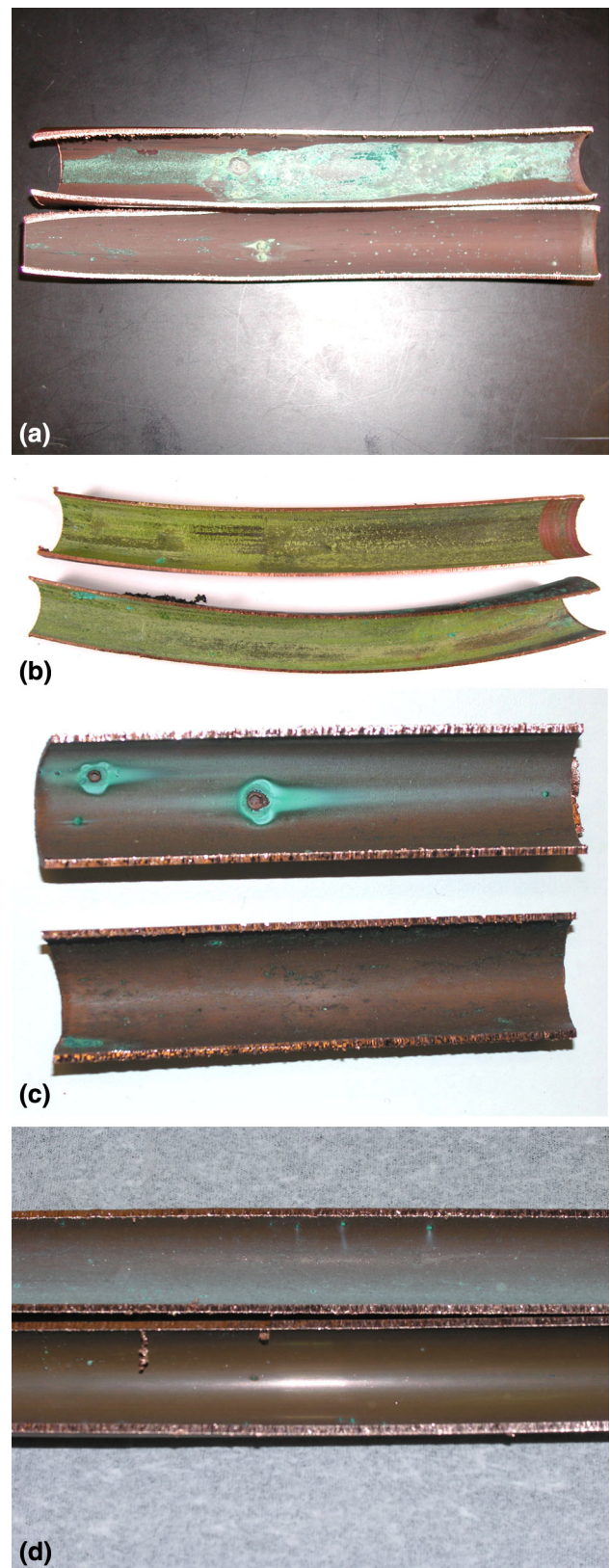


Fig. 1 Internal surfaces of copper pipe sections: (a) dl00255, (b) dl00378, (c) dl00557, and (d) dl00510c

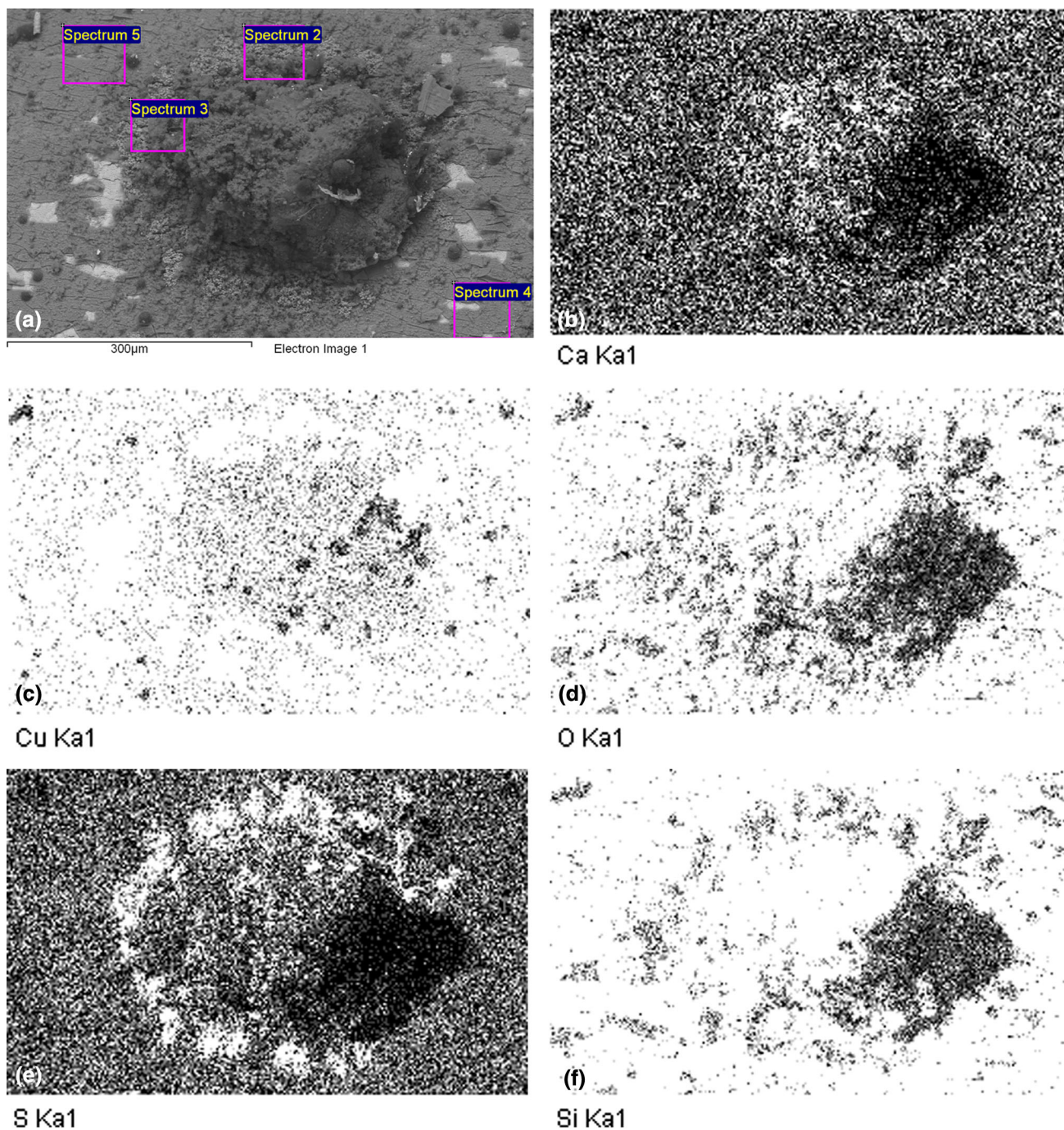


Fig. 2 SEM and corresponding energy dispersive x-ray elemental mapping analysis of the top of a pit cap and surrounding area of the surface of copper pipe section exposed to 1 year of orthophosphate (sample ID dl00255)

entire surface of the pipe including the pit caps (Fig. 2). Silicon levels in the “uniform” portion of the pipe surface (Fig. 2) averaged 11% (by weight) and 8% at the base of the pit cap (Fig. 2; Table 2). Relatively large amounts of sulfur (average 5.5%, Fig. 2) were detected as well, but only at the base of pit caps. The finding suggests that the pit cap is comprised of a sulfate-based solid. Significant levels

of iron (2.4–3.1%) and small amounts of aluminum (0.7%), calcium (0.6%), and magnesium (0.9%) were also detected in all spectra (Table 2). Phosphorus (<0.1%) was not detected on any portion of the analyzed pipe section area. A pit cap was carefully dislodged, and the side in contact with the pipe wall and underlying pipe wall itself were examined. The pipe wall was dominantly copper (average

90.2%) with some oxygen (average 7.2%) (Figs. 3a, S3; Table 2) suggesting a layer of copper oxide (e.g., cuprite, Cu_2O). Silicon (average 1.4%) and chlorine (1%) were also detected in this area. The uniform deposits surrounding the removed cap region were consistent in composition with previous analysis (Fig. 2). The underside of the pit cap was hollow and dome-shaped, and consisted primarily of copper, oxygen, and sulfur (Figs. 3b, S4). Sulfur composed an average of 5.8% of the weight (Table 2) of the internal structure of the cap (Figs. 3b, S4) suggesting that the cap is largely a copper sulfate-based material(s). Aluminum and chlorine were detected as well, but concentrated on the edge suggesting they covered the cap. Phosphorus was not detected in either location. Finally, a cross section of a pit was examined (Fig. 4). The results showed a thin outer layer (layer in contact with bulk water) that was previously described as a uniform cream-colored deposit that was approximately 100 μm thick. The layer consisted dominantly of copper, oxygen, and silicon (10.8%) in composition with small amounts of sulfur, calcium, iron, and chlorine (Table 2; Fig. 4). The internal green and blue material that made up the bulk of the pit cap was comprised dominantly of copper, sulfur (3.8%), silicon (2.6%), and oxygen (Table 2; Fig. 4) supporting the previous conclusion that the pit cap was a copper–sulfate compound(s). The cap covered a thin layer or membrane (Fig. 4). The porous membrane, which separated the cap from the pit, was comprised of copper and oxygen which is, with the presence of cuprite, the material commonly reported to make up the membrane [1]. The pit was broad (~ 2 mm wide) and shallow (~ 0.5 mm deep) in the cross section (Figs. 4, S2c). The images clearly show that localized corrosion attack is occurring below the green and blue corrosion by-product mounds. Copper, oxygen, and elemental chlorine (i.e., chloride) dominated the contents of the pit (Table 2; Fig. 4). Chloride is often associated with pit initiation and growth [1]. It was not possible to ascertain whether the chloride was originally present in the aqueous form or as a copper chloride compound because of dehydration due to drying of the sample prior to analysis.

One Month After Blended Phosphate Addition

Pipe sections collected 1 month after the blended phosphate addition (orthophosphate had been added for 2 years) were analyzed (sample ID dl00378). The pipe sections were covered with a yellow to dark cream-colored solid (Figs. 1b, 5a, b). Green and blue corrosion by-product mounds were randomly spread across the surface. Some of the mounds were covered or partially covered by the cream-colored material (Fig. 5a, b). An image of a large and partially degraded pit cap (~ 8 mm in diameter) reveals the dark red crystalline contents of the pit around

the failure hole that is approximately 1 mm in diameter (Fig. 5a). Figure 5b shows a patch of several corrosion by-product mounds that varied in appearance. Some of the mounds were light blue in color and others green, and some were covered to some degree with the material that made up the uniform portion of the scale. A cross section image of a cut through a pit cap and pipe wall reveals the extent of corrosion attack into the metal (Fig. 5c). The pit cap was approximately 2 mm thick and green and blue in color. At this cross section, the depth of the pit is approximately 2/3 the thickness of the pipe wall. All features of pitting corrosion are present; the pit cap, porous membrane, and pit full of large dark orange cuprite crystals.

Elemental mapping of the surface of the copper pipe section, including a small pit cap (Figs. 6a, S5), showed that the surface was evenly distributed with silicon, oxygen, and copper. Silicon levels in the uniform portion of the pipe surface surrounding (Figs. 6a, S5) and covering the cap (Figs. 6a, S5) averaged 12.6 and 13.7%, respectively (Table 2). Significant levels of iron (2.9–5.3%), aluminum (1.7–1.9%), calcium (0.6–0.8%), and magnesium (1.3–1.5%) were measured in all spectra (Table 2). Also, measurable levels of phosphorus were detected (0.4–0.9%) across these areas showing that the corrosion inhibitor, with time, was being incorporated into the solids that cover the pipe with time. The elemental make-up of the material was similar to solids on the earliest pipe section, except for the presence of phosphorus. Because of the difference in visual appearance between some pit caps, other pit caps on the pipe surface were also examined. The results showed that the elemental composition of the surrounding uniform portion of the solids was nearly identical to previous analysis of other areas (Figs. 6b, S6; Table 2). Interestingly, the cap was covered with phosphorus (Figs. 6b, S6), and silica was nearly absent from the same area. The solid that covered the cap contained largely copper and oxygen, and an average of 7.4% P and 0.4% Si (Figs. 6b, S6). Phosphorus, likely as a copper phosphate compound, either covered or displaced the silicon material. Sulfur was also present at greater amounts (2.1%) than on the surrounding “uniform” portion of the scale. Other elements including calcium, iron, and aluminum (Table 2) were also present but at much lower levels. Phosphorus, presumably from the corrosion inhibitors, was highly concentrated over some pit caps suggesting that it was attracted to sites of localized corrosion.

Elemental analysis of a pit cross section (Figs. 6c, S7) showed that silicon, oxygen, and copper covered the “uniform” portion of the solids on the pipe adjacent to and partially covering the pit cap. The layer was approximately 0.2 mm thick in some areas. The silicon partially covered the pit cap, but was not a significant part of the pit. Phosphorus was found in small areas covering the top of

Table 2 Summary of EDXA elemental compositions of the surface of pipe sections

Figure number	Pipe sample ID	Spectra no.	Elements (wt.%)									
			Oxygen	Magnesium	Aluminum	Silica	Phosphorus	Sulfur	Chlorine	Calcium	Iron	Copper
2	DL00255	2	14.7	0.7	0.5	7.6	<0.1	6.2	0.4	0.6	2.4	66.9
		3	16.6	0.7	0.7	8.9	<0.1	4.8	0.4	0.6	2.9	64.4
		4	21.1	0.9	0.6	10.8	<0.1	0.8	<0.1	0.4	2.5	62.9
		5	22.5	0.5	0.6	11.2	<0.1	0.9	<0.1	0.6	3.1	60.6
3a	DL00255	2	6.9	<0.1	<0.1	1.5	<0.1	<0.1	1.0	<0.1	<0.1	90.6
		3	7.7	<0.1	<0.1	1.3	<0.1	<0.1	0.9	<0.1	0.3	89.7
		4	14.2	0.7	0.5	6.4	<0.1	7.1	0.4	0.5	2.6	67.6
		5	20.0	1.0	0.6	11.8	<0.1	3.3	<0.1	0.7	3.0	59.6
3b	DL00255	2	4.7	<0.1	0.2	0.1	<0.1	0.6	0.9	<0.1	<0.1	93.5
		3	5.6	<0.1	0.1	0.2	<0.1	1.0	1.1	<0.1	<0.1	92.1
		4	9.3	<0.1	0.1	0.5	<0.1	2.8	0.9	<0.1	0.1	86.4
		5	8.6	<0.1	0.1	0.3	<0.1	2.4	1.1	<0.1	<0.1	87.5
4	DL00255	2	0.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	99.1
		3	5.3	<0.1	<0.1	<0.1	<0.1	<0.1	12.2	<0.1	<0.1	82.5
		4	29.8	<0.1	<0.1	10.8	<0.1	2.9	1.2	0.2	0.4	55.1
		5	19.1	<0.1	<0.1	2.6	<0.1	3.8	1.5	0.2	<0.1	73.0
6a	DL00378	2	28.4	1.3	1.8	13.9	0.6	<0.1	<0.1	0.8	3.7	49.5
		3	27.9	1.3	1.8	13.4	0.4	<0.1	<0.1	0.6	2.9	51.6
		4	25.0	1.5	1.7	13.1	0.9	0.3	<0.1	0.8	4.7	52.0
		5	22.9	1.3	1.9	12.1	0.5	<0.1	<0.1	0.8	5.3	55.2
6b	DL00378	2	23.9	<0.1	1.0	0.4	8.0	2.1	<0.1	0.3	0.6	63.8
		3	19.4	<0.1	0.9	0.4	6.7	2.0	0.1	0.3	1.1	69.0
		4	22.9	1.4	2.0	11.9	1.0	0.2	<0.1	0.9	5.9	53.7
		5	23.1	1.7	2.5	11.6	0.8	0.2	<0.1	1.0	8.1	50.9
6c	DL00378	2	3.7	<0.1	0.2	0.2	<0.1	0.2	1.1	<0.1	<0.1	94.6
		3	12.8	<0.1	0.2	0.8	<0.1	<0.1	16.1	<0.1	<0.1	70.1
		4	31.2	<0.1	0.5	1.0	<0.1	10.1	1.2	<0.1	<0.1	56.1
		5	21.3	<0.1	0.7	1.6	3.3	2.6	1.7	<0.1	0.4	68.4
S9	DL00557	4	23.8	0.8	1.1	7.6	4.4	0.3	0.3	0.5	0.8	60.5
		5	24.1	0.5	1.0	5.2	6.9	0.3	0.2	0.6	1.0	60.4
		6	17.5	0.3	0.6	0.4	7.5	0.3	<0.1	0.4	0.8	72.2
		7	16.4	<0.1	0.4	0.5	7.1	0.3	<0.1	0.3	0.9	74.1
7	DL00557	2	29.7	<0.1	0.3	0.2	6.7	5.0	<0.1	<0.1	0.4	57.8
		3	34.3	<0.1	0.4	4.0	5.4	4.7	<0.1	<0.1	<0.1	51.2
		4	21.5	0.4	<0.1	<0.1	5.4	3.8	<0.1	<0.1	<0.1	68.9
		5	22.5	<0.1	<0.1	<0.1	5.6	4.0	<0.1	<0.1	<0.1	67.9
9	DL00509C	2	26.2	<0.1	1.7	0.5	13.1	<0.1	<0.1	0.4	1.8	56.2
		3	26.7	0.4	1.4	0.4	12.9	<0.1	<0.1	0.5	1.7	55.8
		4	28.0	0.6	2.0	10.4	3.3	<0.1	<0.1	0.3	5.1	50.3
		5	29.0	0.6	2.1	11.7	2.1	<0.1	<0.1	0.2	3.8	50.4
10	DL00509C	2	21.3	<0.1	0.3	<0.1	7.0	4.1	<0.1	<0.1	<0.1	67.3
		3	20.3	<0.1	0.3	<0.1	5.5	4.4	<0.1	<0.1	<0.1	69.5
		4	21.0	<0.1	0.8	<0.1	0.6	6.5	<0.1	<0.1	<0.1	71.2
		5	21.0	<0.1	1.2	<0.1	2.1	5.8	0.3	<0.1	<0.1	69.6

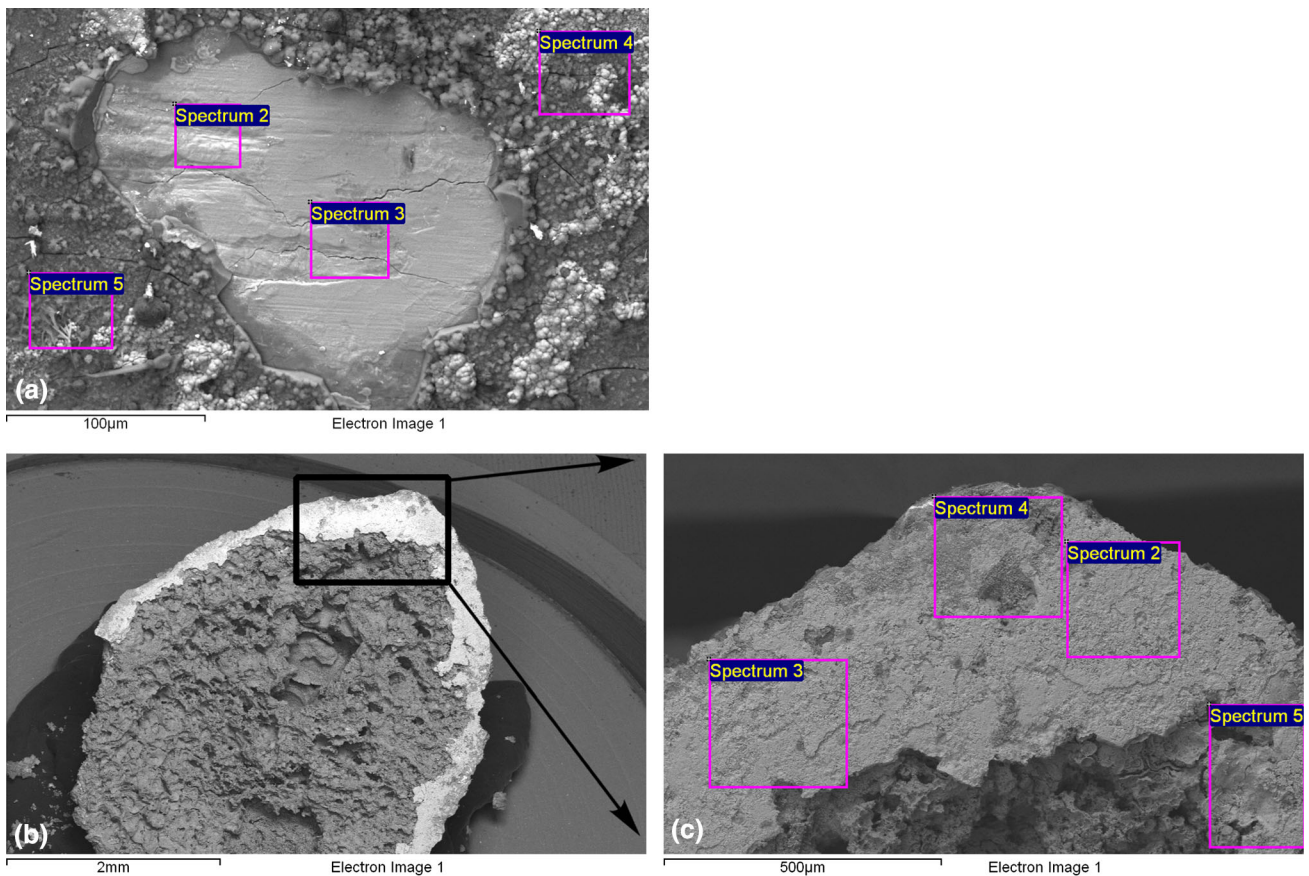


Fig. 3 SEM of (a) pipe surface below a pit cap and surrounding area, (b) the underside of a pit cap removed from a copper pipe section exposed to 1 year of orthophosphate (sample ID dl00255), and (c) an expanded view of (b)

the pit cap. For example, one such region (Figs. 6c, S7; Table 2) contained 3.3% phosphorus which may be somewhat underreported given the area of analysis expanded outside the region of concentrated phosphorus. Phosphorus pockets were generally distinct from silicon, however, it was difficult to precisely determine whether phosphorus displaced or covered the silicon deposits. The bulk of the internal cap material was comprised of copper (56.1%), sulfur (10.1%), and oxygen (31.2%) (Figs. 6c, S7; Table 2). Elemental chlorine (i.e., chloride) (16.1%) and copper (70.1%) dominated the material in the pit.

Nine Months After Blended Phosphate Addition

Pipe sections collected 9 months after the blended phosphate addition were analyzed (sample ID dl00557). The pipe surface appeared dark orange with very little in the way of cream-colored solid as seen on prior pipe sections (Fig. S8a). Green and blue corrosion by-product mounds (or remnants of dislodged mounds) were randomly spread across the pipe surface (Fig. S8). Streaks of green material were also present around the mounds (Fig. S8). An image

of an area where a large mound was dislodged (Fig. S8b) shows the pit and the hole or location of failure that is nearly 1.5 mm in diameter.

SEM examination of the surface of a corrosion by-product mound shows the rough features of the material (Fig. S9). EDXA elemental mapping analysis of the cap surface (Fig. S9) showed that copper, phosphorus, and oxygen were relatively uniformly deposited across the cap surface. Silicon was detected in areas surrounding the pit cap. Analysis of the elemental composition on the pit cap (Fig. S9; Table 2) showed the average amounts of phosphorus and silicon were 7.3 and 0.5%, respectively. The area adjacent to the cap contained 5.7% P and 6.4% Si. Iron, aluminum, and calcium were also present at low levels.

Visual and microscopic examination of the underside of the pit cap revealed the domed appearance of the cap that covers the pit, which is common with all of the caps examined in this work (Fig. 7). Elemental mapping shows that the band of material at the base of the cap that was in contact with the pipe wall is dominated by copper, oxygen, phosphorus, sulfur, and silicon (Fig. 7). Elemental spectra collected in the area in contact with the pipe wall (Fig. 7; Table 2) showed that the average copper, oxygen, and

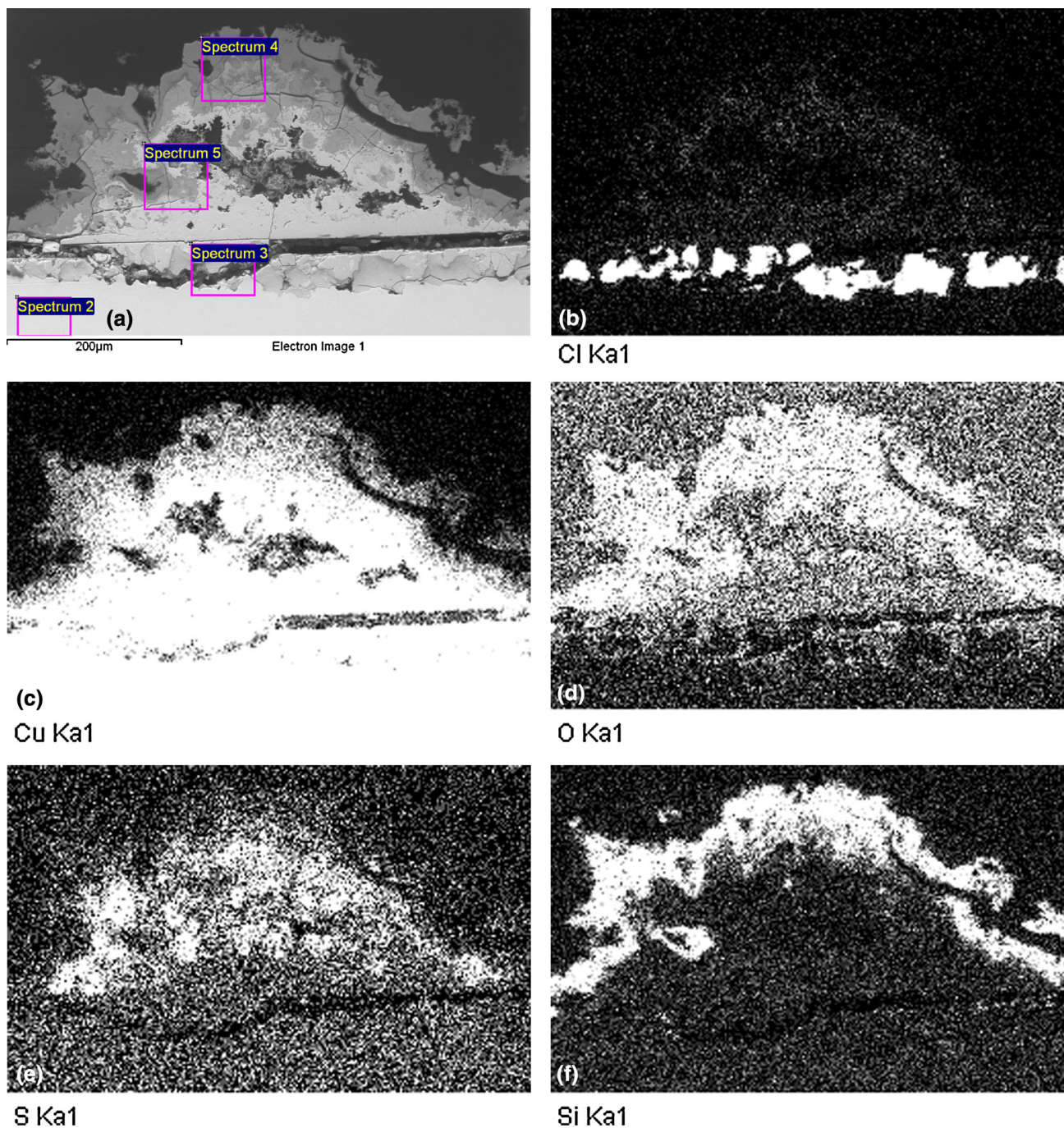


Fig. 4 SEM and corresponding energy dispersive x-ray elemental mapping analysis of the cross section of a pit from a copper pipe section exposed to 1 year of orthophosphate (sample ID dl00255)

phosphorus quantities were 54.5, 32.0, and 6.2%, respectively. Sulfur, silicon aluminum, and iron were all detected as well. The accumulation of phosphorus in this region is of particular significance because the region is at or near the cathode reaction that drives the localized corrosion and degradation of the copper pipe wall. The copper–phosphorus solid also covered the internal dome of the cap (Fig. 7; Table 2).

One Year After Blended Phosphate Addition

Pipe sections were collected 1 year after addition of blended phosphate and analyzed (sample IDs dl00509 and dl00510). The internal pipe surface was similar in appearance and physical features to other pipes removed at earlier times into treatment (Fig. 1d). Much of the surface was dark orange to brown in color. Blue and cream-colored

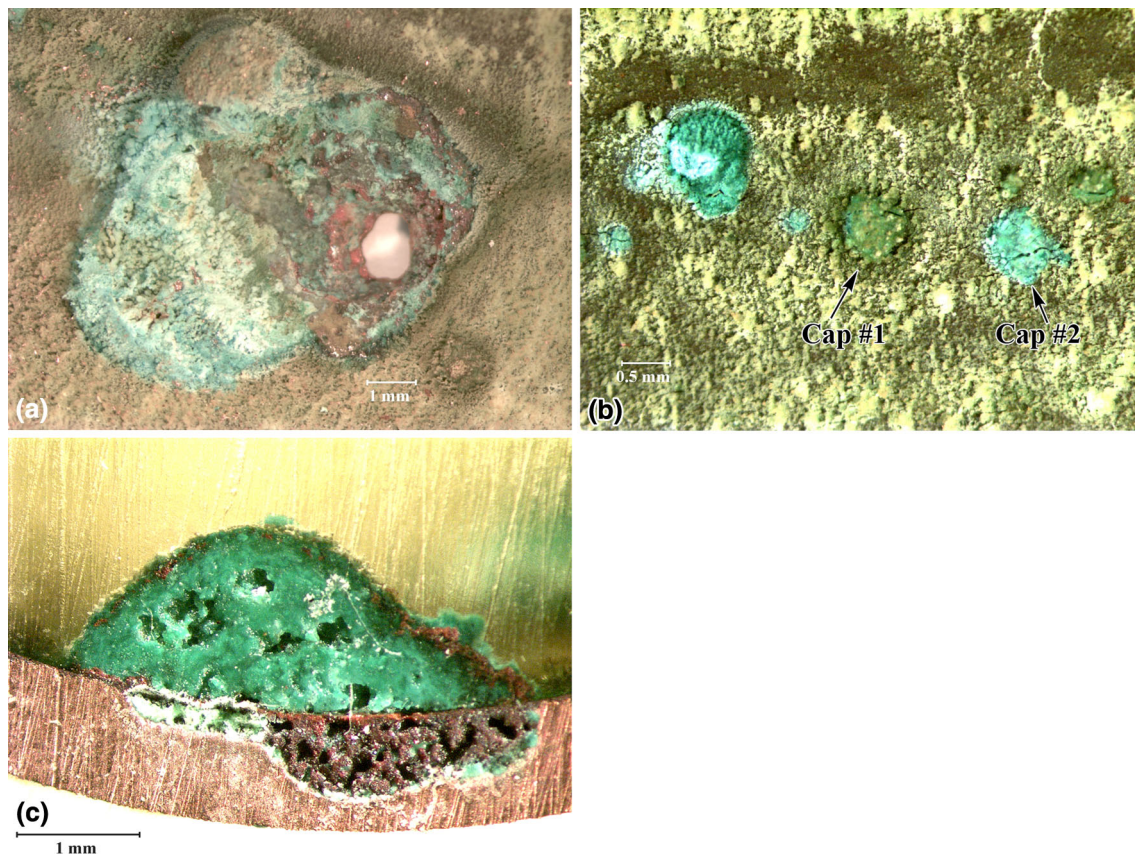


Fig. 5 Features of pitting corrosion attack on pipe section exposed to 1 month of blended phosphate (sample ID d100378): **(a)** close-up of internal surface of pipe including a portion of the pit cap and view of

hole, **(b)** several local corrosion mounds on pipe surface, and **(c)** cross section showing pit cap, porous membrane, and pit

deposits were deposited relatively uniformly across portions of the pipe surface, and green- and blue-colored corrosion by-product mounds of various sizes were randomly spread across the pipe surfaces. An orange- to brown-colored surface (Fig. 8a) that, upon close examination, appeared to be perforated in some locations was revealed below the corrosion by-product mounds (presumably pit caps). The underside of the cap consisted of a mix of blue and green solids, and a well-defined ring of white material was present at the base (Fig. 8b). The white ring outlined the domed central portion of the cap (difficult to appreciate in the micrograph).

Elemental mapping analysis of the surface of the copper pipe section, including a small pit cap (Fig. 9), showed that the surface composition varied with location. The relatively uniform layer of material was dominated by silicon, oxygen, and copper. Silicon levels in the uniform portion of the pipe surface (Fig. 9) averaged 11% (Table 2). Significant levels of iron (3.8 and 5.1%), aluminum (2.0 and 2.1%), calcium (0.2 and 0.3%), and magnesium (0.6%) were also detected across uniform solid spectra (Table 2). This composition was very similar to the composition of the uniform material

in previous pipes except the amount of phosphorus increased to 2.6% on average with time. The pit cap was totally covered with a relatively concentrated layer of phosphorus (and copper and oxygen) (Fig. 9), and silica was either absent or covered by the phosphorus-containing material. Specifically, the material (Fig. 9; Table 2) contained an average of 13.0% phosphorus, which was higher than past samples, and only 0.5% silicon. It also contained copper and oxygen.

The underside of a pit cap was examined by SEM and EDXA analysis (Fig. 10). As with before, the cap was hollow toward the center—presumably in the region directly above the growing pit—which again suggests that the water was corrosive (e.g., low pH). Elemental mapping in this region provided details about the composition of the cap and the white ring at the base of the cap. Copper, sulfur, and oxygen with phosphorus in regions were identified throughout the base of the cap. Interestingly, the white ring was dominantly phosphorus, oxygen, and copper. Specifically, the white ring contained 7.0 and 5.5% phosphorus, respectively (Fig. 10; Table 2). The actual concentration of the ring is greater than the reported values because the scanned region is wider than the band. The white band was examined under greater

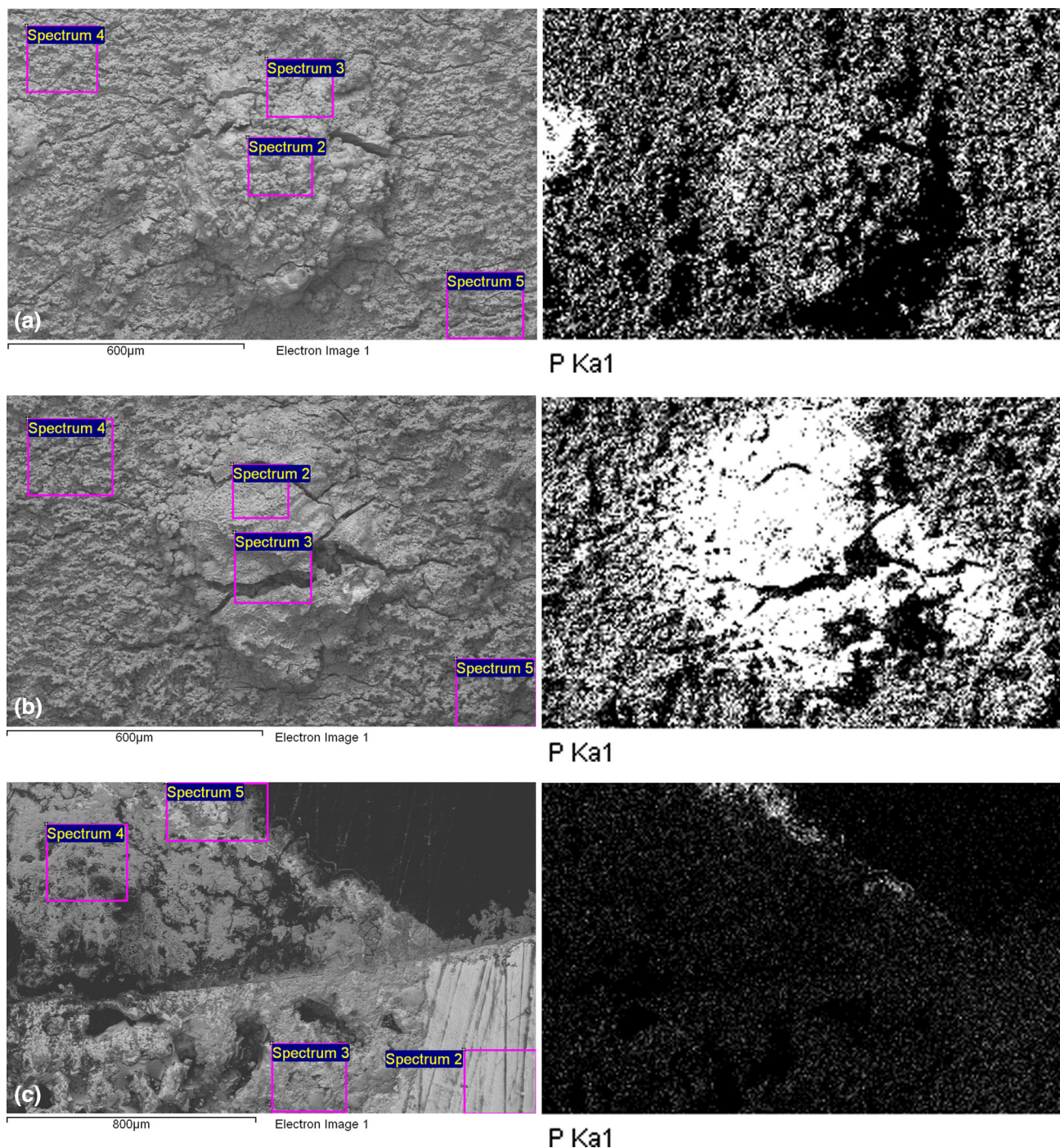


Fig. 6 SEMs and corresponding energy dispersive x-ray mapping analysis of phosphorus on the surface of copper pipe section exposed to 1 year of orthophosphate (sample ID dl00378): (a) the top of a pit cap and surrounding area, (b) another pit cap, and (c) cross section through pit cap

magnification and showed the well-defined shape of the solids in the band (Fig. 8c). Solids were long (3–4 µm) and elliptical in shape. Closer examination of the solids showed the ratio of Cu:P:O in the solid was almost exactly 2:1:3.4 and contained between 13 and 17% phosphorus.

Elemental analysis of a pit cross section (Fig. S10) showed that the pit was dominantly made of copper,

oxygen, and sulfur. There was also a relatively large amount of phosphorus spread more uniformly across the cap cross section. This observation was different from the distribution of phosphorus in sample dl00378 where phosphorus was primarily limited to the surface of the cap. Silicon was not detected in the analysis region. Elemental chlorine (i.e., chloride) and copper dominated

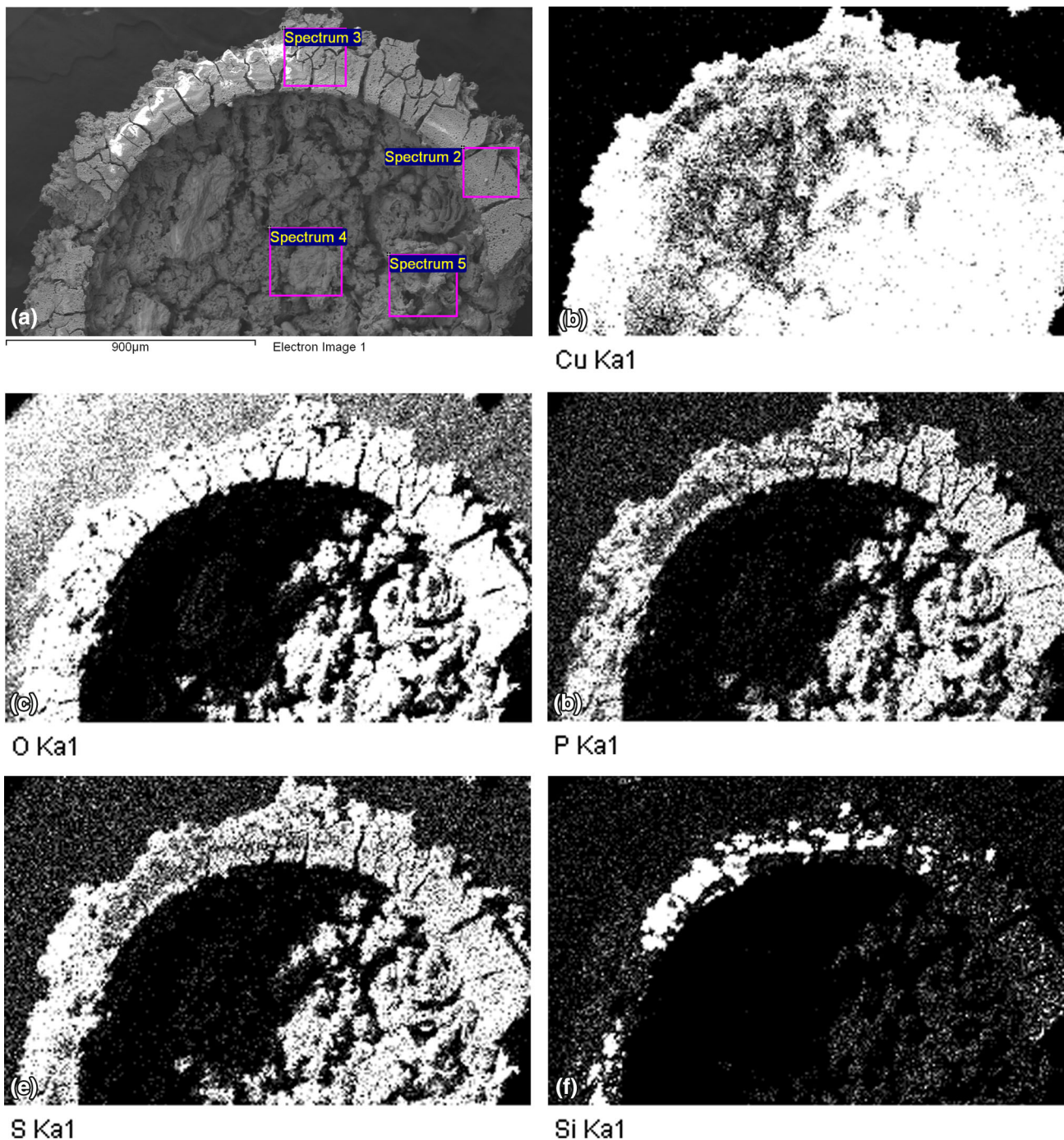


Fig. 7 SEM and corresponding energy dispersive x-ray analysis elemental mapping analysis of the underside of a pit cap removed from a copper pipe section exposed 9 months after blended phosphate addition (sample ID dl00557)

the material in the pit. Phosphorus did not appear to migrate into the pit.

Discussion and Conclusions

The impact of phosphate as a function of time on the interior surface of failed copper drinking water distribution

pipes removed from household plumbing was studied. Duration of phosphate addition did not have an obvious effect on the visual appearance and physical features of the interior surface of copper pipes. Many pipes were covered in varying degrees by a relatively uniform cream-to-light-yellow shaded solid. Relatively small mounds of blue and green corrosion by-products were randomly dispersed across the pipe surfaces. The mounds were often covered

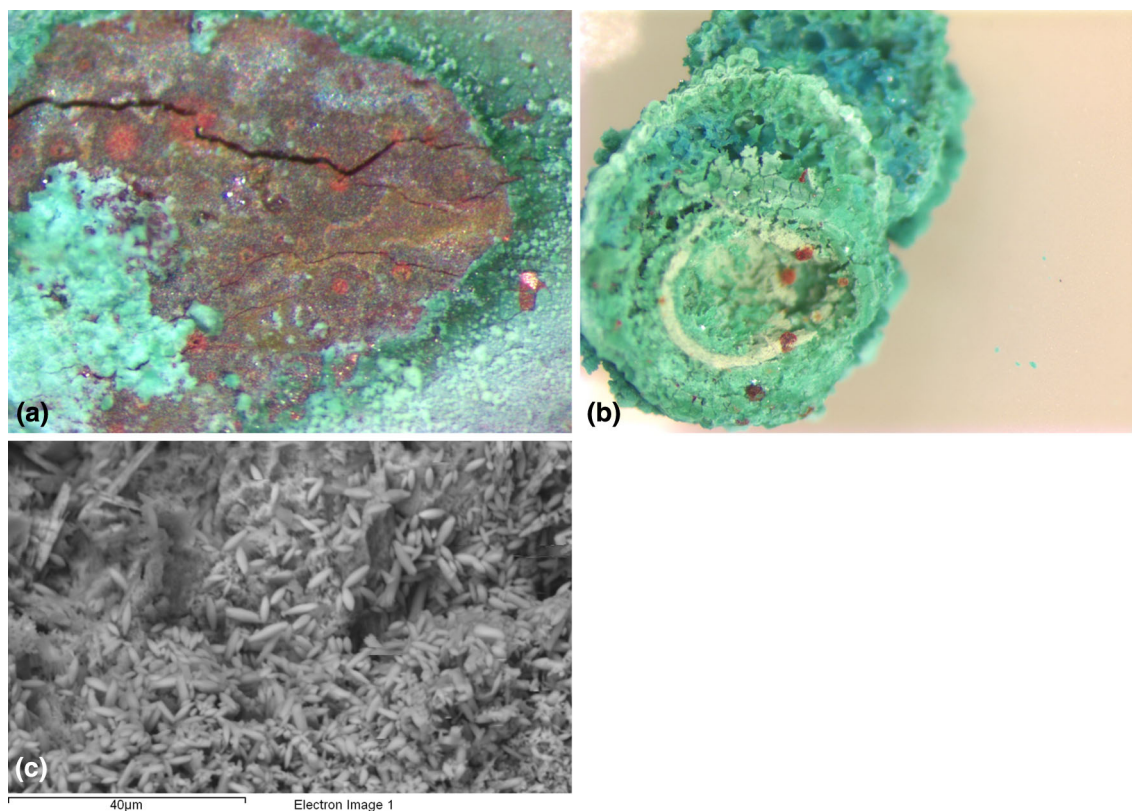


Fig. 8 Stereomicrographs of (a) copper pipe surface below a pit cap and (b) the underside of a removed pit cap, and (c) SEM of white solid ring on underside of pit cap (sample ID dl00509c, approximately 1 year after ortho-polyphosphate blend addition)

with the uniform material, and mounds or remnants of the mounds always covered the location of pinhole leaks. Some degree of pitting corrosion was observed in every case where cross-sectional analysis through a corrosion by-product mound or pit cap and pipe wall was performed. Features commonly associated with localized corrosion including a perforated membrane and a pit full of dark orange cuprite crystals was present below pit caps.

EDXA elemental analysis clearly revealed the role of phosphates on the copper pipe surfaces and localized corrosion with time (Fig. S10). Orthophosphate did not appear to have a measurable impact on the pipe surface based on the observation that phosphorus was not detected on the copper pipe surface after 1 year of application. The observation was somewhat unexpected. However, there are a number of possible explanations, such as: phosphorus levels on the copper pipe surface were below the detection limit of EDXA (<0.1%); orthophosphate was not consistently dosed to the water at the desired level; orthophosphate in the distribution system water did not “carry-out” to the sampled home; or measurable phosphorus accumulation takes longer than 1 year. Copper, silicon, and oxygen were identified as the major components of the “uniform” solid that covered the pipes. Aluminum, iron, calcium, and magnesium were also present but in much lower amounts. Pit caps consisted of

copper, sulfur, and oxygen, and pits contained copper, chlorine (i.e., chloride), and oxygen. In general, the elemental make-up of the pipe surface features (other than phosphorus) was independent of length of exposure to phosphate addition.

The amount of phosphorus on the surface of copper pipes increased dramatically with time following the addition of blended phosphate to the finished water. Phosphorus in the uniform scale averaged 0.8% after only 1 month addition. The most interesting and significant observation was the localized concentration of phosphorus (average of 7.4%) over the pit caps. The analysis could not determine whether phosphorus displaced or covered the silica-rich layer that typically covered pit caps prior to the addition of the blended phosphate chemical, but it was clear that phosphorus was associated with copper (i.e., a copper phosphate or polyphosphate solid phase). The amount of phosphorus increased from 2.6 to 13% in the uniformly deposited solids and over the pit cap, respectively, after 1 year of blended phosphate addition. Phosphorus also migrated through the pit caps and deposited at the base of the cap as a distinct copper–phosphorus compound. XRD analysis did not identify a specific copper phosphorus compound(s).

The exact reason phosphorus accumulated around areas of localized copper corrosion is not known, but a

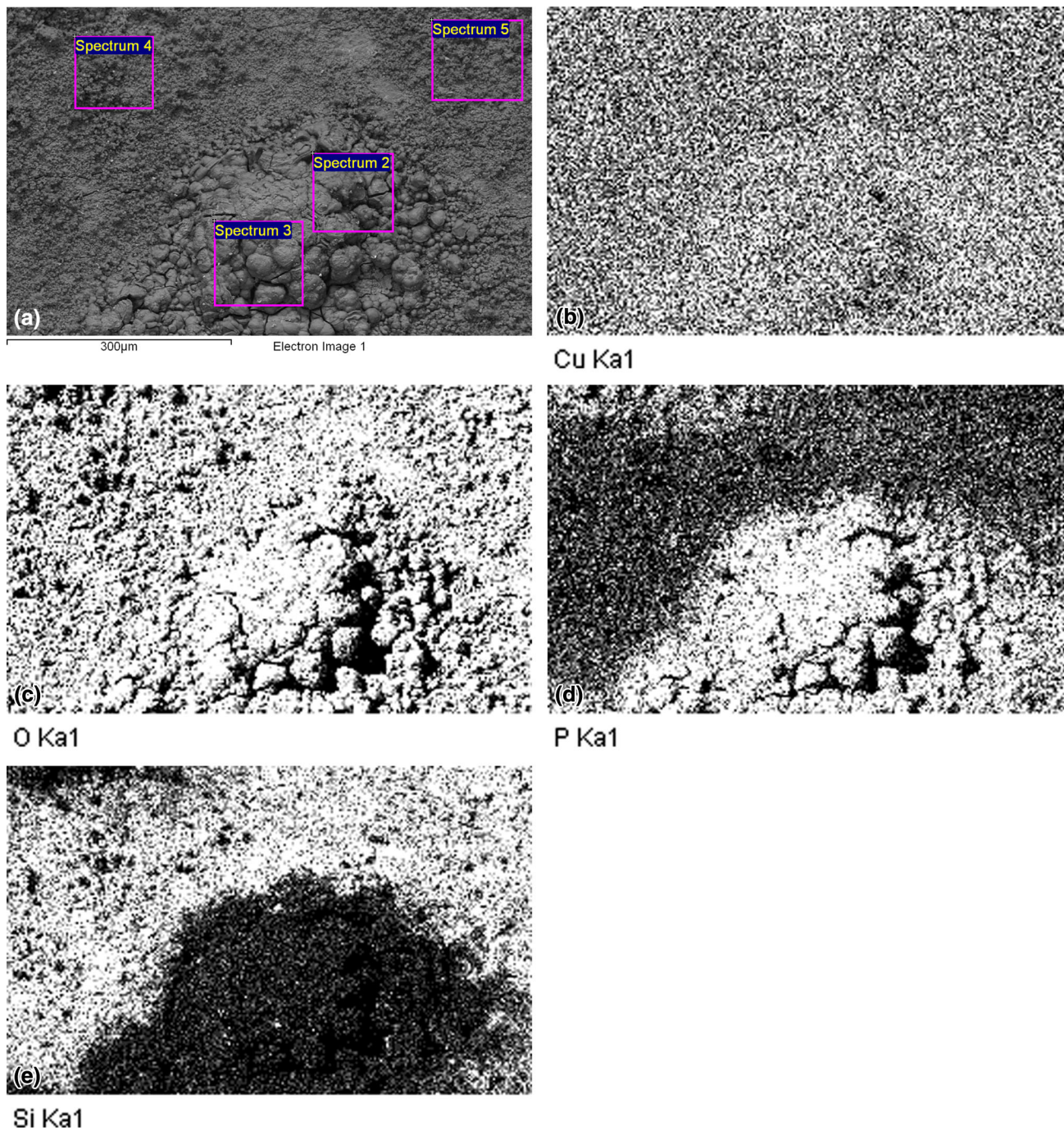


Fig. 9 SEM and corresponding energy dispersive x-ray analysis elemental mapping analysis of the cross section of a pit from a copper pipe section exposed to blended phosphate (sample ID dl00509c)

reasonable explanation can be proposed. An influx of anions to the anodic region of a pit is necessary to counter the generation of copper cations and maintain electroneutrality in the anodic region. This is fundamental knowledge, and explains the presence of chlorine (i.e., chloride) and sulfur (i.e., sulfate) in and around the copper pits. Orthophosphate and polyphosphates are negatively charged ions in water, and also expected to be

attracted to and accumulate near the corroding copper anode. Copper orthophosphate minerals are relatively insoluble over a broad pH range compared to copper sulfate and chloride minerals, and cupric hydroxide [23]. The accumulation of copper and phosphate ions in the region would result in precipitation of copper phosphate compounds and could reasonably explain the build-up of phosphorus over pits. Phosphate ions could also displace

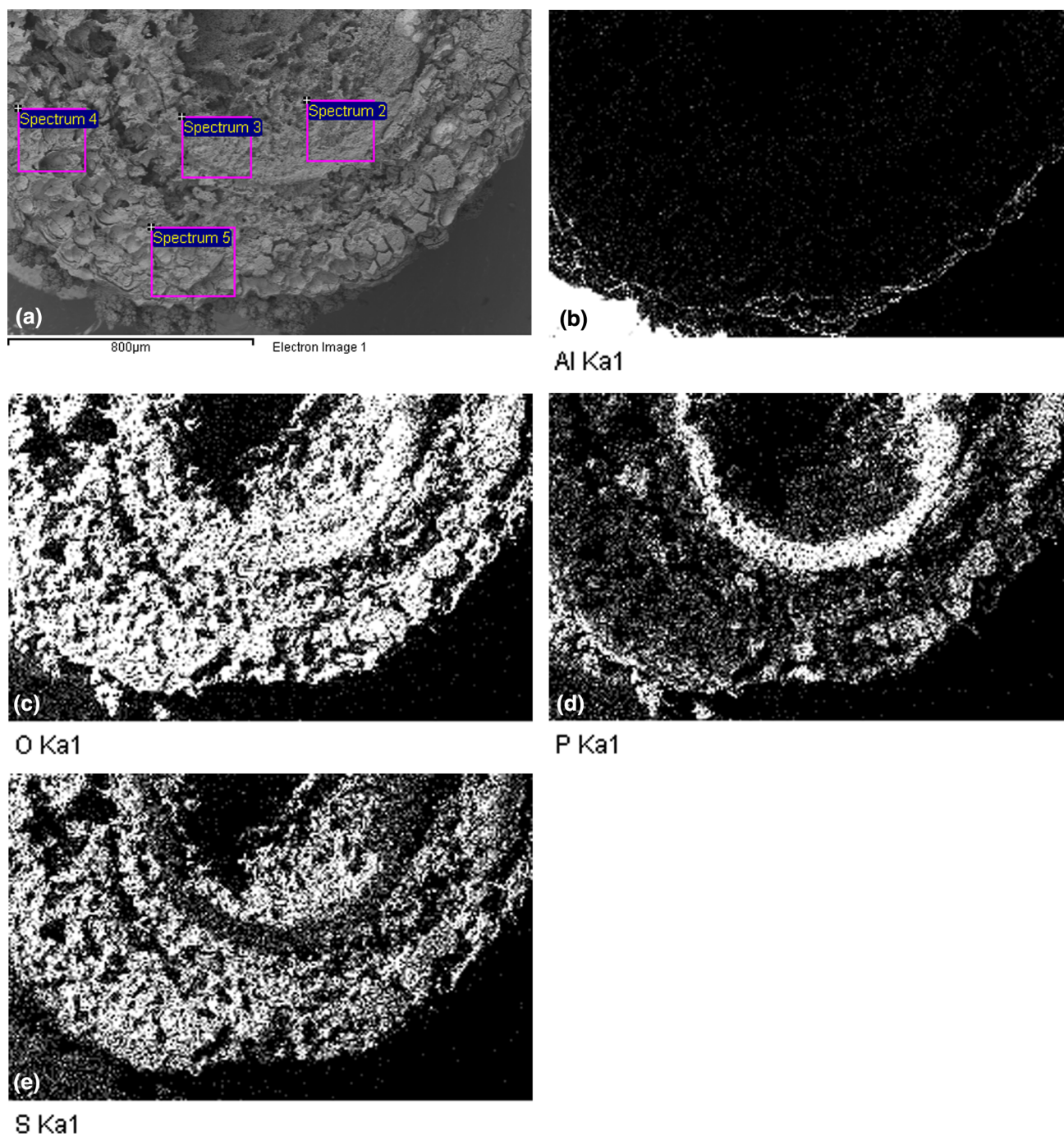


Fig. 10 SEM and corresponding energy dispersive x-ray analysis elemental mapping analysis of the underside of a pit cap removed from a copper pipe section exposed to 1 year of orthophosphate (sample ID dl00509c, 9 months after ortho-polyphosphate blend)

less electronegative ions like chloride which are critical to pit propagation.

The obvious practical question is whether the observed concentration of copper–phosphorus compounds around pits as well as other parts of the copper pipe surface is beneficial toward reducing the pinhole leak problem in the test utility and other systems. The utility has reported a gradual decrease in plumbing permits to a “baseline” level

and a large drop-off in customer complaints following the addition of phosphate. However, as already noted, accurately assessing trend changes in consumer pinhole leak reports is complicated by many factors, and beyond the scope and objective of this project but the subject of a follow-up investigation. Nonetheless, the scientific observations made during this study provide insight into pitting corrosion mechanisms and control. Potential beneficial

roles of phosphorus toward mollifying pinhole leak episodes in situ are various. First, relatively insoluble copper phosphates formed, which may have prevented diffusion of oxygen, copper, and other ions that enter the pit or nearby cathodic region of the corrosion cell. Second, reducing the solubility of copper in the region will reduce the influx of chloride and sulfate to the region. Orthophosphate and polyphosphate accumulation may have the same benefit.

Finally, the role of orthophosphate versus polyphosphates is unclear, but worthy of further research. Detectable levels of phosphorus on pipe surfaces were not observed until after polyphosphate was included in the chemical formulation. Possible explanations for the absence of phosphorus on pipe sections removed prior to blended phosphate addition have already been proposed. The presence of phosphorus on copper pipes shortly after polyphosphate addition may not be a coincidence. The role of polyphosphate and the associated observations made in this study provide ample promise to warrant additional research.

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