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Copper-Tube Corrosion

in Domestic-Water Systems

Identifying and mitigating the seven forms of corrosion

To control the corrosion of copper tubes and fittings exposed to domestic waters, one first must understand its cause, as mitigation techniques are not universal. Through more than 1,500 investigations conducted over 25 years, the authors identified seven sources of copper-tube corrosion in domestic-water systems:

- Soldering-flux-induced pitting attack.¹
- Hydrogen-sulfide-induced pitting attack.
- Erosion corrosion.^{2,3,4}
- Cuprosolvency.^{5,6,7}
- Concentration-cell corrosion.^{8,9}
- Chemistry-related cold-water pitting.^{5,10,11,12,13}
- Chemistry-related hot-water pitting.^{14,15}

This article will describe each of these forms of corrosion and discuss methods of mitigating them.

Soldering-Flux-Induced Pitting Attack

Occurring most often in cold-water lines, but also known to occur in infrequently used hot-water lines, soldering-flux-induced pitting attack almost always is associated with the use of an unusually aggressive flux and/or excessive amounts of flux. Once initiated, the propagation of pits is facilitated by the natural presence of dissolved oxygen in conveyed water.

Containing porous, reddish-brown cuprous oxide (Cu_2O), flux-induced pits are covered with relatively voluminous, friable tubercles of green-colored copper-corrosion products (Photo A). Typically, the tubercles consist of basic copper carbonate (i.e., malachite) and/or copper chloride(s).

Flux-induced pits tend to occur preferentially along relatively narrow bands that are nearly parallel to the longitudinal axes of tubes and fittings (i.e., along the “ghosts” of flux runs). Often, these bands are covered with tubercle ridges (see the top tube half-section in Photo A), rather than distinct hemispherically shaped tubercles. Flux-induced pits also often occur preferentially on the periphery of petrolatum-base flux residues/runs, which often exist on water-side surfaces when plumbing technicians apply flux excessively. When flux is applied excessively, globules of solder also can be found on water-side surfaces of tubes and fittings. Although



PHOTO A. Soldering-flux-induced pits covered with friable green tubercles of copper-corrosion products. The tube-wall perforations (see arrows) and most of the pits exist along relatively narrow bands, which are nearly parallel to the longitudinal axes of the tubes (i.e., along the “ghosts” of flux runs).

flux-induced pitting can be expected at or near poorly soldered connections, pitting has been known to occur more than 8 ft from fittings.

Soldering-flux-induced pitting can be confirmed using energy dispersive spectroscopy (EDS). Chlorides in major amounts—and, sometimes, zinc (from the soldering flux)—can be detected in pits or on the edges of pits (Figure 1). Copper chloride exists with Cu_2O at pit sites. This is understandable, as soldering fluxes commonly contain activating chlorides, such as ammonium chloride, zinc chloride, tin chloride, and/or hydrochloric acid.

Soldering-flux-induced pitting can be avoided by stipulating that plumbing technicians use industry-standard materials and practices when installing copper-tube systems. Fluxes should satisfy the requirements of ASTM B813, *Standard Specification for Liquid and Paste Fluxes for Soldering of Copper and Copper Alloy Tube*.¹⁶ Soldered connections must be made in accordance with ASTM B828, *Standard Practice for Making Capillary Joints by Soldering of Copper and Copper Alloy Tube and Fittings*,¹⁶ and “The Copper Tube Handbook.”¹⁷

There are no known methods of mitigating flux-induced pitting attack. Typically, systems are replaced after four or five leaks.

Hydrogen-Sulfide-Induced Pitting Attack

Small quantities of dissolved hydrogen sulfide (H_2S) in water can cause pitting of many metallic materials. Although the threshold concentration for copper is not known, quantities as low as 0.020 mg per liter have resulted in perforations.

Typically, domestic water containing H_2S is obtained from well supplies. Sulfide is a natural constituent of many well waters, resulting from underground sulfate-reducing-bacteria activity and/or general bacteria decomposition.

H_2S -induced pitting occurs randomly on water-side surfaces of copper tubes and fittings (Photo B). The pits typically contain porous, dark-reddish-brown-to-nearly-black Cu_2O and are overlaid with friable green tubercles of copper-corro-

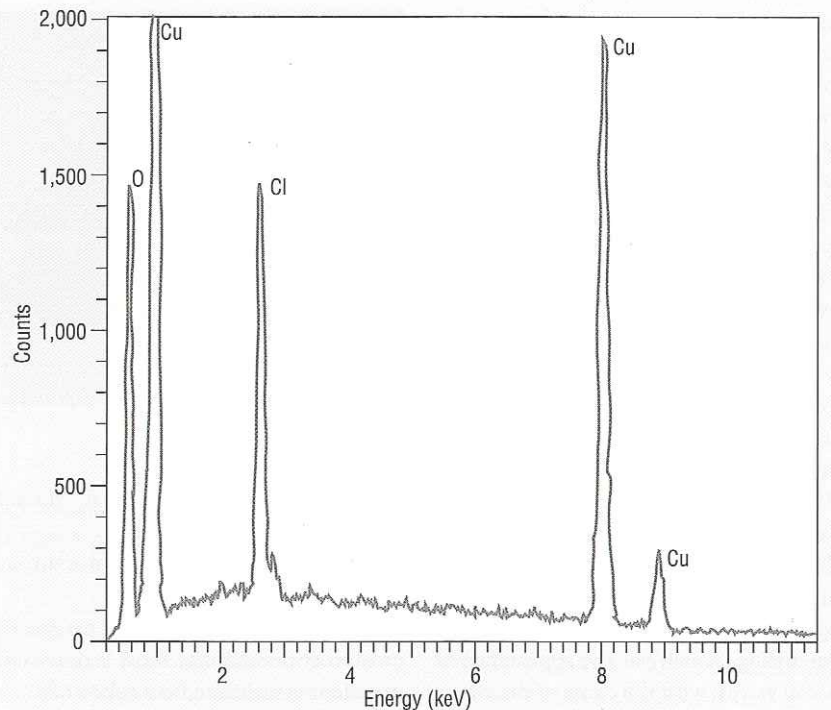


FIGURE 1. Energy dispersive spectroscopy normally reveals large amounts of chloride at soldering-flux-induced pit sites.

sion products. Most often, the tubercles consist of copper sulfate, which sometimes is admixed with black copper sulfide(s). Regardless of the composition of the tubercles, black, loosely adherent, porous layers of copper sulfide(s) are associated with pitting attack. The presence of these corrosion products can be verified using EDS and microchemical analysis (MCA).

H_2S can be removed from water sup-

plies through a number of techniques,^{18,19} such as aeration in a forced-draft tower. Sulfide is removed by the scrubbing action of air and by oxidation. Lowering the pH of water greatly reduces the size of aerating equipment required.

Erosion Corrosion

Erosion corrosion (i.e., accelerated attack related to localized high-veloc-



PHOTO B. Hydrogen-sulfide-induced pits overlaid with friable green to black tubercles of copper-corrosion products. Loosely adherent and porous layers of copper sulfide have broken free from the upper two tube half-sections.

ity/turbulent water inside tubes and fittings) of copper tubes and fittings normally is associated with circulating domestic-hot-water (DHW) systems.

Erosion corrosion can be recognized readily (Photo C). Areas of attack typically are grooved and essentially free of residual corrosion products. Affected areas normally are bright and shiny, like a new penny. This is understandable, considering the erosion phase of this rapid, repetitive process removes copper-oxide films from copper surfaces. Often, the U-shaped pits in areas of attack are distinct enough that the direction of water flow can be determined. The orientation of the pits gives the impression of "horses walking upstream." Lengthwise sections of tube normally reveal undercutting, which has the appearance of ocean waves, with the crests of the waves facing the direction of water flow.³

In circulating hot-water systems, erosion corrosion often is associated with naturally soft waters and waters softened to a near-zero hardness, particularly waters containing appreciable amounts of dissolved oxygen and/or dissolved carbon dioxide (CO₂). Erosion corrosion is facilitated by water temperatures greater than 140 F and flow rates above 4 to 5 fps. Erosion corrosion can be especially severe at water temperatures above 160 F, at which point black cupric oxide (CuO) forms instead of reddish-brown Cu₂O. CuO appears to be much less resistant to erosion corrosion than Cu₂O is. Erosion corrosion also can be facilitated by the presence of abrasive suspended solids (e.g., iron oxide and/or sand). Often, erosion-corrosion damage is restricted to locations where water flow makes multiple changes in direction over relatively short distances.

Poor workmanship is a leading cause of erosion-corrosion failures. This includes:

- Unreamed cut tube ends.
- Globules of solder on water-side surfaces.
- Dents in tubes and fittings.
- Tubes not fully inserted into fittings prior to soldering.
- Tubes "cocked" in fittings.
- Tubes not cut squarely.

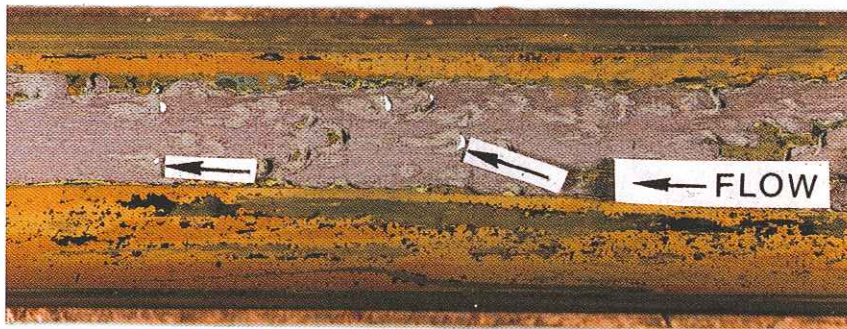


PHOTO C. U-shaped pits and associated tube-wall perforations (see arrows) in a localized product-free area are distinct enough that the direction of hot-water flow can be determined.

- Improperly installed flared fittings.

- Disrupted flow and excessive turbulence in other locations.

Of workmanship-related causes of erosion corrosion, the most serious and prevalent is unreamed cut tube ends.

Erosion corrosion can be mitigated by keeping water velocity below 4 to 5 fps, eliminating abrasive suspended solids from circulating water, and maintaining water temperature below 130 F.⁴

Excessive velocity in circulating systems often is associated with oversized circulating pumps and/or undersized tubes and fittings. Sometimes, these conditions result from design deficiencies or changes to designs during installation.

Abrasive solids aggravate erosion corrosion by destroying protective Cu₂O film. The repetitive process of forming and destroying the film erodes copper tube and causes failures. The source of abrasive solids in water often is iron oxide(s) from the corrosion of steel hot-water heaters/storage tanks upstream of copper-tube systems. This condition usually can be corrected with protective coatings, generally in conjunction with cathodic protection of the ferrous-based materials.

In aerated domestic-water systems in which water must be circulated at temperatures greater than 120 to 130 F, water velocities should be controlled below the recommended 4 to 5 fps. When velocities are required to exceed 4 to 5 fps or aggressive domestic waters must be circulated at temperatures above 130

F, tubes and fittings made of 90-10 copper nickel should be considered.⁴

When erosion corrosion occurs in cold-water lines, the cause almost always is unusually high (greater than 80 psig) water pressure, which results in water velocities in excess of 7 to 8 fps, and/or poor workmanship. Erosion corrosion in cold-water systems can be mitigated by keeping water velocities below the industry-recommended 8 fps and by using industry-standard practices during installation.¹⁷

Cavitation, a special form of erosion corrosion, occurs when vapor/gaseous bubbles form at low pressure and collapse/implode at high pressure, producing very high localized pressures (shock waves) that destroy copper's protective tarnish film and create boundary-layer water temperatures that are much higher (above 160 F) than those of the water being conveyed. Typically, cavitating copper is distinguished by the absence of residual corrosion products and the presence of bright, sponge-like, rounded pits (Photo D).

Cuprosolvency

Cuprosolvency, sometimes referred to as the "blue/green" water concern, describes the slow general corrosion (i.e., uniform attack) of copper water tubes and fittings. It can result in stained plumbing fixtures and somewhat elevated copper levels in water following periods of zero flow. Although cuprosolvent water can be annoying, it is not known to have culminated in a tube- or fitting-wall perforation.

Cuprosolvency occurs when water-



PHOTO D. A tube-wall perforation (see arrow) in a localized area of severe cavitation. Surface heating caused the formation of black cupric oxide where cavitation had not occurred.

side surfaces of copper tubes and fittings do not form or completely form a naturally protective Cu_2O film, developing instead a thin, loosely adherent, flocculent-type layer of blue to blue-green copper-corrosion products⁷ (Photo E). Typically including copper hydroxide, these products are formed during periods of water stagnation.

Cuprosolvent water typically is very soft (near-zero hardness), with a pH of less than 7 and a low alkalinity. In general, the pH is less than neutral because of the presence of dissolved CO_2 .⁵

Cuprosolvency usually is self-correcting, once a sufficient supply of water flows through a line. The water's dissolved oxygen enables the copper to form a naturally protective Cu_2O film.

When cuprosolvency is persistent, mitigation can be accomplished by raising the pH of the water to about 8 through the addition of chemicals, such as sodium hydroxide and calcium hydroxide. At individual residences, cuprosolvency can be corrected by installing neutralizing filters.

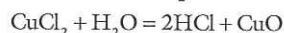
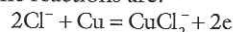
Flux-induced cuprosolvency involves the slow, nearly uniform dissolution of copper, rather than the development of pits.

Concentration-Cell Corrosion

The form of concentration-cell corrosion associated with copper domestic-water systems is oxygen differential. Often, it is referred to as underdeposit corrosion because deterioration occurs

preferentially, in the form of pits under deposits, where the oxygen content of water is lower than it is immediately adjacent to the deposits.

The localized corrosion process can be especially rapid, such as when chloride anions migrate to anodic sites under deposits and react with metal to form metal chlorides, which react with water (hydrolyze) to form hydrochloric acid. The reactions are:



The source of deposits on tubes and fittings almost always is suspended solids in the water conveyed. Often, these deposits consist of iron oxides and/or silica/sand (Photo F). It is not unusual for the source of iron oxides to be the corrosion of cast-iron/ductile-iron mains used to distribute water or galvanized-steel service lines used to connect buildings to water mains. Iron oxides also can result from the oxidation of natural constituents in water (e.g., iron bicarbonate). When deposits consist primarily of silica/sand, the cause normally is the overpumping of a well or a deteriorating concrete or cement-lined water main. In rare cases, the source of deposits is post-precipitation of colloids leaving the water-treatment plant.

Once the source of corrosion-causing deposits is identified, suspended solids in water usually can be eliminated. For example, the corrosion of cast-iron/ductile-iron mains and galvanized-steel service lines can be mitigated cost-effectively with water treatment,⁸ normally by the water purveyor. Suspended solids can be removed with filtration,⁸ either at the treatment plant or the affected building/residence. Improved dwell time at treatment plants can eliminate the post-precipitation of suspended solids in water-distribution systems.

Chemistry-Related Cold-Water Pitting

Chemistry-related cold-water pitting of copper tubes and fittings, sometimes referred to as nodular or Type 1 pitting, is associated with low-pH, high-alkalinity well water and combinations of well and surface supplies. Normally, the pit-

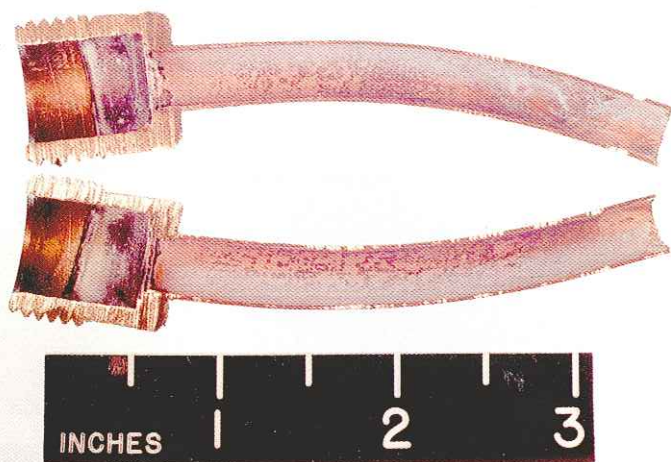


PHOTO E. A loosely adherent flocculent-type layer of blue-tinted copper-corrosion products on the water-side surface of a tube.

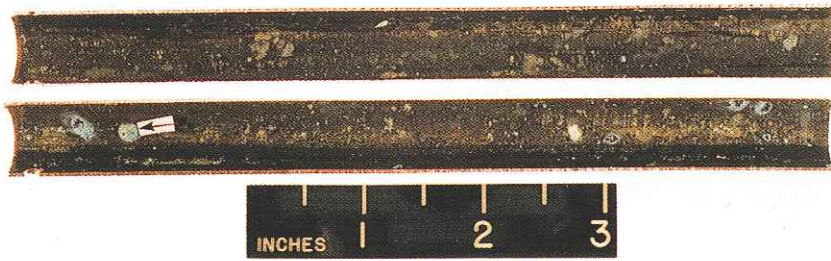


PHOTO F. Concentration-cell corrosion in the form of pitting attack under the thicker layers of hydrated hematite and silica deposits on the water-side surface of a cold-water line. The perforation through the tube wall (see arrow) is covered with a friable tubercle of green copper-corrosion products.

ting occurs in cold-water lines or infrequently used hot-water lines. The corrosive agent is dissolved CO_2 .

The randomly occurring pits contain porous, reddish-brown Cu_2O and are overlaid with discrete, friable, relatively voluminous tubercles of green copper-corrosion products (Photo G). Typically, EDS and MCA reveal that the tubercles consist primarily of basic copper carbonate.¹¹ EDS sometimes shows that copper chlorides coexist with the Cu_2O in the pits. Copper in areas where localized pitting has not occurred will be covered with a protective tarnish film of Cu_2O , which, in general, will be overlaid with a thin layer of green deposits (typically, malachite), the source of which is the pitting of copper upstream.

Chemistry-related cold-water pitting is distinguishable from flux-induced pitting by the randomness of its occurrence. The pitting is not located preferentially along the "ghosts" of flux runs or on the periphery of sticky petroleum-base flux residues.

Waters commonly associated with chemistry-related cold-water pitting normally have a pH of 7.0 to 7.7 and contain 25-mg-per-liter-plus dissolved CO_2 , along with dissolved oxygen. These waters are common in the Midwest and New Mexico, where waters have high alkalinity. T.E. Larson and A.M. Buswell²⁰ presented a technique for calculating dissolved- CO_2 content:

$$\log(0.88 + Kl) + \log(\text{total alkalinity}) + 0.05 - \text{pH} = \log \text{CO}_2$$

where:

$\log(0.88 + Kl)$ is the temperature factor, which is 6.35 at 55 F

The higher the dissolved- CO_2 content, the greater the potential for chemistry-related cold-water pitting.

The most viable and cost-effective means of overcoming chemistry-related cold-water pitting in copper domestic-water systems is to reduce dissolved- CO_2 content.^{10,11,12,13} Chemistry-related cold-water pitting is relatively rare in municipal water supplies because purveyors routinely treat the water to raise pH and reduce dissolved CO_2 . Raising a water's pH to about 8 while reducing its CO_2 content to less than 5 mg per liter will mitigate the concern. Environmentally acceptable chemicals for achieving this objective include caustic soda, lime, and soda ash, which usually are added at treatment plants. For private residences, the same objective usually can be achieved by installing a neutralizing filter.

A study by Fred Fink at Battelle Laboratories compared waters that caused pitting with those that did not. The study revealed that water prone to causing pitting often contains more than 15-mg-per-liter chloride and more than 17-mg-per-liter sulfate, with the

sulfate-to-chloride ratio often in excess of 3. Based on more than 100 investigations of chemistry-related cold-water pitting of copper tubes and fittings, there is no reason to believe manufacturing-related carbon films or other films on copper surfaces are a factor in pitting attack.¹¹

Chemistry-Related Hot-Water Pitting

Domestic hot waters containing relatively small amounts of iron, manganese, and/or aluminum have been associated with hot-water pitting of copper tubes and fittings. There also is reason to believe a silicon-containing constituent could be involved. The quantities of aluminum, manganese, and iron required to initiate pitting attack are believed to be as low as 0.10,¹⁴ 0.03,¹⁵ and 0.10 mg per liter, respectively. Generally, hot-water pitting associated with these metals is a concern when water has been heated to temperatures in excess of 160 F and black CuO exists on hot copper surfaces.

Typically, hot-water-induced pits contain porous, reddish-brown Cu_2O and are covered with friable, relatively voluminous tubercles of green copper-corrosion products (Photo H). EDS and MCA usually reveal that the tubercles consist primarily of copper sulfate. Often, EDS will detect small amounts of the pit-initiating metal in the tubercles. Rarely will EDS detect chloride-containing products in the pits.

Where pitting has not occurred and copper is covered with a thin layer of CuO , a friable, loosely adherent layer of brown (Photo I) or brown-black (Photo H) deposits is common. The deposits

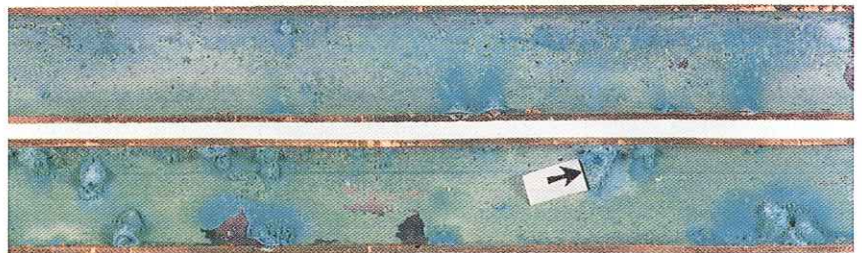


PHOTO G. Tubercle-covered, corrosion-induced pits on the water-side surface of a tube that conveyed a domestic cold water containing appreciable amounts of dissolved carbon dioxide in conjunction with dissolved oxygen.

will contain varying amounts of aluminum, iron, and/or manganese. EDS in the immediate vicinity of the pits will provide the insight necessary to identify the metal(s) primarily responsible for the pitting attack.

Iron and manganese appear to initiate pitting attack through the deposition of highly cathodic iron oxide (especially hydrated hematite) and highly cathodic manganese dioxide, respectively, on hot copper surfaces, especially at locations where temporary defects in the copper-oxide layer exist. Once initiated, pits propagate by microgalvanic corrosion and concentration-cell corrosion of the oxygen-differential form. The role of aluminum in the pitting process is less clear because investigators have been more interested in solving a practical concern than providing fundamental research.¹⁴ The pitting process could involve the deposition of aluminum sulfate and its hydrolysis to aluminum hydroxide on hot copper surfaces, which then leads to the localized destruction of copper's passive film.

Regardless of the corrosion mechanism, copper pitting initiated by waters containing iron, manganese, and/or aluminum is facilitated by the heating of conveyed waters to higher-than-necessary temperatures and by the presence of sulfate in the waters.

Concentrations of manganese and/or iron in waters often can be reduced at treatment plants. Manganese- and iron-removal systems are available for this purpose. For example, coagulation, flocculation, and precipitation or filtration can remove colloidal iron. Sometimes, the iron content of water can be reduced sufficiently by mitigating the corrosion of hot-water heaters/storage tanks, cast-iron/ductile-iron mains, and/or galvanized-steel service lines upstream of copper-tube systems. Reducing the temperature of water to 120 to 130 F and adding properly blended sodium-silicate/organic-polyphosphate inhibitors to water also have been known to mitigate hot-water corrosion.

Hot-water pitting associated with the presence of aluminum in water has been mitigated by raising the pH of the water



PHOTO H. Chemistry-related-hot-water-induced pits covered with friable tubercles of green copper-corrosion products. Loosely adherent layers of brown hydrated hematite deposits cover black cupric oxide on the water-side surface of a hot-water line.

to 8.5 while reducing the aluminum content to less than 0.1 mg per liter. Often, aluminum content, as well as sulfate content, can be reduced to an acceptable level by simply reducing the amount of aluminum sulfate used for coagulation at the treatment plant and/or ensuring adequate coagulation, settling, and filtering of water before it is distributed. Reducing the temperature of water from 165 F to 130 F also has been known to correct the pitting concern. Indeed, not only has lowering the temperature reduced the rate of reaction, there is reason to believe that pits do not initiate at the lower temperature. Recent studies suggest that the aluminum content of domestic hot water can be reduced to acceptable levels by avoiding the use of sacrificial aluminum-alloy anodes in hot-water heaters.

Conclusion

The seven basic forms of copper corrosion in domestic-water systems can be

mitigated cost-effectively provided:

- Water purveyors distribute quality products (e.g., waters that do not contain unacceptable amounts of H₂S, dissolved CO₂, suspended solids, iron, manganese, and/or aluminum).
- Copper-tube systems are designed properly (e.g., in circulating systems, velocities do not exceed 4 to 5 fps).
- Copper-tube systems are installed properly (e.g., installed using the general guidelines presented in ASTM Standard Practice B828¹⁶ and "The Copper Tube Handbook,"¹⁷ without the use of excessive amounts of flux and/or unusually aggressive flux).
- Copper-tube systems are operated within design parameters (e.g., DHW temperatures do not exceed 120 to 130 F, and measures are taken to prevent the corrosion of water heaters/storage tanks).

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PHOTO I. A tube-wall perforation (see arrow) covered with a friable tubercle of green copper-corrosion products. The cupric oxide on the tube surface is covered with a relatively thick, loosely adherent layer of brown deposits from the hot water conveyed. EDS will reveal that the deposits contain significant amounts of aluminum.

References

- 1) Myers, J.R., & Cohen, A. (1994). Soldering flux-induced pitting of copper water lines. *Materials Performance*, 33, 62-63.
- 2) Knutsson, L., Mattsson, E., & Ramberg, B.E. (1972). Erosion corrosion in copper water tubing. *British Corrosion Journal*, 7, 208-211.
- 3) Obrecht, M.F., and Myers, J.R. (1973, June). The forms of corrosion in potable water piping (pt. I). *Heating/Piping/Air Conditioning*, pp. 57-62.
- 4) Obrecht, M.F., & Myers, J.R. (1973, August). Performance and selection of materials for potable hot water service. *Heating/Piping/Air Conditioning*, pp. 53-59.
- 5) Lyman, W.S., & Cohen, A. (1972). Service experience with copper plumbing tube. *Materials Performance*, 11, 48-53.
- 6) Gilbert, P.T. (1969). *Dissolution by fresh waters of copper from copper pipes*. Proceedings of the Society for Water Treatment and Examination, 15, 165-186.
- 7) Page, G.C. (1963). Contamination of drinking water by corrosion of copper tubes. *New Zealand Journal of Science*, 16, 349-387.
- 8) During, E.D.D. (1988). *Corrosion atlas: a collection of illustrated case histories* (case histories 06.05, 15.01). New York: Elsevier Science Publishers.
- 9) Obrecht, M.F., & Myers, J.R. (1973, July). The forms of corrosion in potable water piping (pt. II). *Heating/Piping/Air Conditioning*, pp. 33-37.
- 10) Rambow, C.A., & Holmgren, R.S. (1966). Technical and legal aspects of copper tube corrosion. *Journal of the American Water Works Association*, 58, 347-353.
- 11) Myers, J.R., & Cohen, A. (1995). Pitting corrosion of copper in cold potable water systems. *Materials Performance*, 34, 60-62.
- 12) Cohen, A., & Myers, J.R. (1987). Mitigating copper pitting through water treatment. *Journal of the American Water Works Association*, 79, 58-61.
- 13) Cohen, A., & Myers, J.R. (1993). Water treatment to mitigate corrosion of copper plumbing system. *Materials Performance*, 32, 43-45.
- 14) Tuntura, P., & Ylasaari, S. (1968). *A special case of the pitting corrosion of copper in a hot water system*. Paper presented at 5th Scandinavian Corrosion Congress, Copenhagen.
- 15) Holden, W.S. (Ed.). (1970). *Water treatment and examination* (pp. 425-426). London: J. and A. Churchill.
- 16) ASTM International. (2002). *Annual Book of ASTM Standards* (vol. 02.01). West Conshohocken, PA: ASTM International.
- 17) CDA. (2004). *The copper tube handbook*. New York: Copper Development Association. Available at http://www.copper.org/resources/pub_list/pdf/copper_tube_handbook.pdf
- 18) Wells, S.W. (1954). Hydrogen sulfide problems in small water systems. *Journal of the American Water Works Association*, 46, 160-170.
- 19) Foxworthy, J.E., & Gray, H.K. (1958). Removal of hydrogen sulfide in high concentrations from water. *Journal of the American Water Works Association*, 50, 872-878.
- 20) Larson, T.E., & Buswell, A.M. (1943). *Calcium carbonate saturation indexes and alkalinity interpretations*. Illinois State Water Survey Circular 22.

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