Technical Note

Pitting Corrosion of Copper in Cold Potable Water Systems

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Copper tubing in potable water systems is highly resistant to corrosion. However, pitting attack will occur in tubing carrying cold water with an aggressive chemistry (typically, pH of 7.0 to 7.7 and dissolved carbon dioxide of at least 25 mg/L). The most cost-effective method for preventing this pitting is altering the water chemistry by raising the pH and reducing the carbon dioxide content.

Each year, about one billion linear feet (1/3 billion meters) of copper water tubing is installed in U.S. water service and distribution systems. This is equivalent to about 190,000 miles (315,000 km) of tubing in hot and cold potable water systems. Since statistics began to be gathered in 1946, about 40 billion feet of copper tube have been installed in water service and distribution systems for U.S. buildings. That is more than 7.4 million miles (12.3 million km), or about 31 times the distance from the earth to the moon.

On average, the Copper Development Association (CDA) investigates 42 incidents involving copper water tubes each year. Although many more corrosion incidents probably occur, the small number accurately reflects the quantitative relationship between the enormous amount of copper water tube in use and the infinitesimal number of corrosion problems related to it.

Table 1 indicates the relative importance of copper tubing pitting corrosion vs all types of corrosion attack in plumbing installations for 1988 through 1994. The data show that in 1993, for instance, cold water pitting was only fourth in importance as a cause of failure; in 1994, no cold water pitting incidents were investigated by the CDA. The distribution of failures remained essentially unchanged for all seven years.

Pitting corrosion of copper water tube has been studied extensively since publication of Campbell's paper in 1950.[1] CDA's Copper Data Center database contains more than 200 documents testing Campbell's original conclusions.

Characteristics of Cold Water Pitting

Cold water pitting is characterized by corrosion-induced pits on the water side surface of the tube (or fittings) which are covered with friable tubercles (nodules) of green copper corrosion products (arrow, Figure 1). Typically, the tubercles consist of basic copper carbonate (malachite)[2,3] which, depending on the water chemistry, may be mixed with calcium carbonate, basic copper sulfate, copper chloride(s), or basic copper phosphate. The corrosion-induced pits under the tubercles contain crystals of porous reddish-brown cuprous oxide, with cuprous chloride typically at the bottom of the pits.[4,5]

A protective tarnish film of reddish-brown cuprous oxide invariably covers areas of the inside surface of the copper tube where pitting has not

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TABLE 1
CDA Field Investigations of
U.S. Service Incidents Involving Copper Plumbing Tube

	Year						
Corrosion Cause	**1988**	**1989**	**1990**	**1991**	**1992**	**1993**	**1994**
Cold water pitting	7	9	5	14	5	9	0
Concentration cell	2	1	1	10	3	12	6
Flux corrosion	7	10	8	12	10	22	10
Underground corrosion	1	7	1	5	8	3	0
Green water	1	2	1	2	3	3	0
Erosion–corrosion	4	7	2	15	9	11	3
Sulfide attack	1	0	0	2	2	5	1
Stress corrosion cracking	3	1	1	1	1	0	0
Hot water pitting	2	0	3	3	0	6	3
Workmanship	1	2	1	1	2	3	1
Galvanic	0	1	0	0	0	0	0
Total	29	40	23	65	43	74	24

occurred. The cuprous oxide is generally overlaid with a thin, friable layer of loosely adherent malachite; the malachite undoubtedly deposits from the water and is associated with the pitting of copper upstream in the system.

Cold water pitting can be distinguished from soldering flux-induced pitting by the random occurrence of the pits. The pits are not located along relatively narrow bands parallel to the longitudinal axes of the tubes and fittings, as is generally observed when soldering flux residue is responsible for the pitting.[6]

Influence of Water Chemistry

All investigations of cold water pitting conducted by the CDA concluded that the dominant factors promoting cold water pitting are the aggressive characteristics of the water conveyed by the tube.

In the United States, copper tube pitting is almost exclusively a cold water phenomenon; Campbell designated this form as "type 1" pitting.[2,7]

With only rare exceptions, type 1 pitting is associated with the presence of well water in less urban areas of the country, especially in arid regions. More than half the pitting cases that have come to CDA's attention occurred west of the Mississippi River, with most in Southern California, Arizona, and Utah. The phenomenon rarely occurs in surface waters or in well supplies in other regions of the country.

Aggressive Water Chemistries

It is generally agreed that water aggressiveness is a critical factor in pitting. For example, dissolved oxygen and dissolved carbon dioxide clearly are involved in the pitting mechanism, and pitting waters typically contain chlorides.[8-10] Cuprous chloride normally is found in the bottoms of the pits. Very likely, propagation of the corrosion-induced pits is facilitated by hydrolysis of the cuprous chloride to cuprous oxide and hydrochloric acid. There is also reason to believe that, once initiated, pitting is facilitated by the presence of sulfate in the water.[9]

Experience has shown that a pitting-type water typically has a pH of 7.0 to 7.7 and contains more than 3 mg/L dissolved oxygen, 25 mg/L dissolved carbon dioxide, 15 mg/L chloride, 17 mg/L sulfate, less than 25 mg/L nitrate, more than 26 mg/L silica, and less than 4 mg/L potassium. The sulfate-to-chloride ratio usually exceeds 3-to-1. For waters in the pH range 7.1 to 7.6, the presence of more than 100 mg/L magnesium sulfate in the water has also been associated with pitting attack.

Pit initiation caused by dissolved carbon dioxide is consistent with the fact that carbon dioxide acts as a cathodic depolarizer when copper is exposed to cold water.[5,7] Depolarization of the cathodes on the copper surfaces shifts the corrosion potential of the metal in the positive (noble) direction until it exceeds the critical potential for pitting attack (for example, about 170 mV relative to a saturated calomel electrode).[4,7] Once initiated, pitting is facilitated by the dissolved oxygen in the water.

Deleterious Film Controversy

Some investigators have claimed that a form of manufacturing-related "deleterious film," such as carbon, must exist on the copper surface for pit initiation to occur.[1,2,8,11] Others have insisted that deleterious films are not important and certainly not necessary, and that their role in the pitting process has been overemphasized.[9,12-14] The incidence of attack involving deleterious films is extremely low compared with the number of copper tubes and fittings in service. Also, such deleterious films could not be identified during laboratory investigations of more than 100 cold water

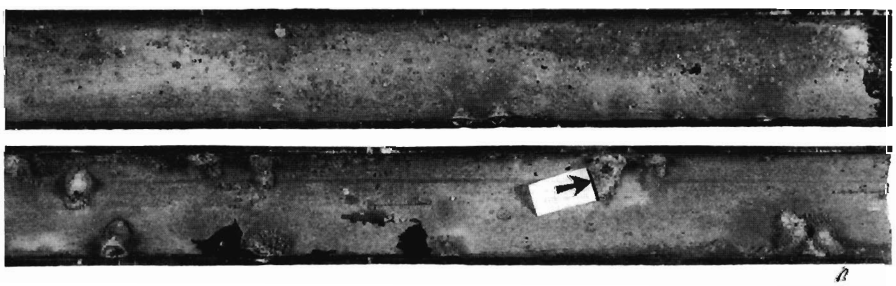

FIGURE 1
The corrosion-induced pit associated with the perforation through the tube wall was covered with a relatively voluminous tubercle of friable green-colored copper corrosion products (for example, see arrow). Original magnification 1.3x, reduced 23%.

pitting incidents conducted by the authors.

Avoiding Cold Water Pitting

The most viable and cost-effective solution to overcoming water chemistry-related cold water pitting corrosion of copper plumbing is to treat the offending aggressive water so the free carbon dioxide content is reduced to a sufficiently low level.[10,15-17]

Carbon dioxide must remain in the water to keep the corrosion potential of the copper more positive than the critical value; otherwise, the pits cannot propagate. Dissolved carbon dioxide cannot exist in waters having a pH greater than about 8.3. Experience has shown that raising an aggressive water's pH to about 8.0 while reducing its dissolved carbon dioxide content to less than about 5 mg/L will successfully mitigate cold water pitting.

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