New Research Pinholes in

A noted researcher reports that he has made a breakthrough in addressing an ongoing corrosion problem.

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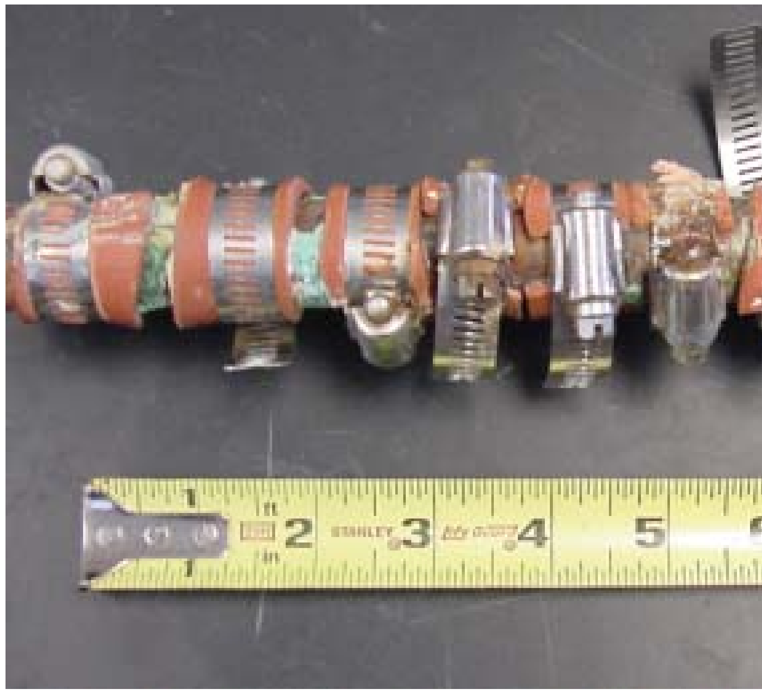


Could the infamous pinhole puzzle be solved?

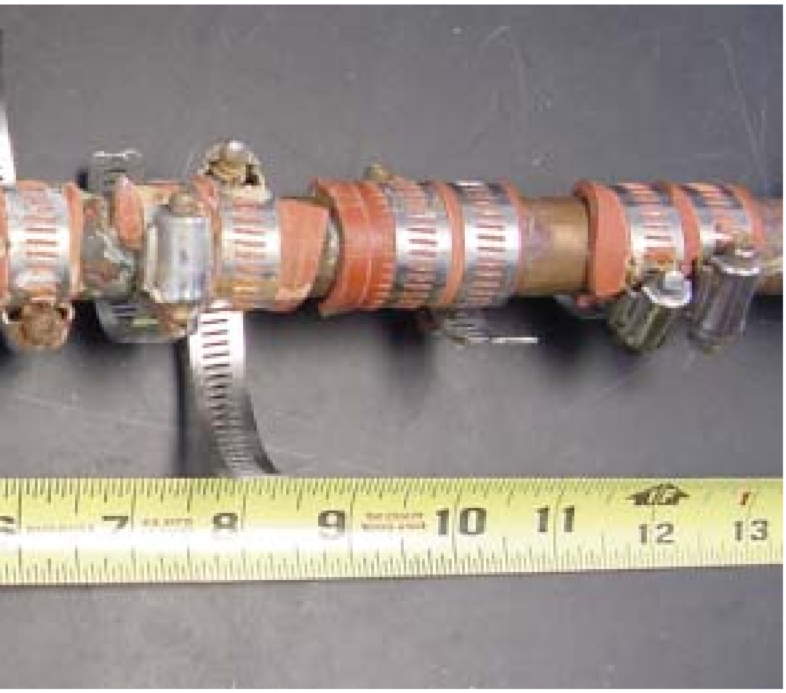
Regular *MP* readers may recall a December 2002 feature article discussing the problem of pinhole leaks forming in copper tubing in residential water distribution systems.[1] The article states that the leaks would form spontaneously in homes and apartment buildings, surprising unsuspecting residents and in many cases leading to destructive and expensive results. Some experts have hypothesized that the leaks, which became prevalent in the suburban Washington, D.C., area and elsewhere in the late 1990s and earlier this decade, were caused by tubing defects. Others have blamed stray current, lightning, or microbiologically influenced corrosion (MIC). The previous MP article focused on a third explanation: changes in the U.S. Environmental Protection Agency's (EPA's) water treatment rules, specifically the "Lead and Copper Rule [LCR]" calling for lower levels of natural organic matter (NOM), lead, and copper in drinking water.[2] Those espousing this school of thought cited earlier laboratory experiments demonstrating that NOM acts as an anodic inhibitor to copper and that metals corrode very differently in waters with NOM than in those without it. The main drawback to this theory, however, was that there was no known case in which anyone had replicated the copper pitting phenomenon as it actually occurs. The corrosion engineer interviewed in the article has informed MP that this barrier has been overcome.

A Turning Point

"This was the first experiment to replicate pitting of copper tube in the laboratory as it occurs in practice," says Marc Edwards, Professor of Civil and Environmental Engineering at the Virginia Polytechnic Institute and State University (Virginia Tech) (Blacksburg, Virginia). "During the test, eight holes were formed in a 1-ft [0.3-m] section of pipe in just 1 year using a potable water chemistry that anyone can synthesize in the laboratory. The solution was based on the water chemistry associated with outbreaks of copper pitting that have occurred in Maryland, Washington, D.C., and other areas of the country."

Edwards explains that the experiment showed that the water chemistry produced partly as a result of the LCR—a combination of aluminum, free chlorine, and pH greater than 8.0—initiated

May Explain Copper Tubing



This copper pipe, from the D.C. WASA system, is largely hidden by clamps placed over individual pinhole leaks. There have been cases in which such leaks have occurred at a frequency greater than one per inch of copper tube, and hundreds of leaks have occurred in individual buildings. New research from Virginia Tech concludes that aggressive water, partly an effect of federal water quality regulations, causes this problem. Photo courtesy of Marc Edwards, Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia.

pitting. "We have proven that the combination of higher pH, low organic matter, aluminum, and free chlorine in water can cause pinhole leaks of copper," he says. In addition, the research found that aluminum in water catalyzed the cathodic reaction between copper and chlorine after being deposited on the copper surface. "This is a major driver of the copper pitting attack," he says, adding that the findings were confirmed in a subsequent third-party study funded by the Copper Development Association (CDA) (New York, New York). It should be noted that previous studies have identified aluminum (in hot water) as the cause of pitting in copper.[3]

Edwards also suspects that using chloramines instead of free chlorine with elevated pH, low NOM, and aluminum can cause copper pitting as well; he cautions, however, that this has not yet been confirmed. Chloramines are produced by combining chlorine and ammonia (NH_3). Weaker yet more stable than chlorine, chloramines remain in a water utility's distribution system longer than chlorine; the disinfectants thus enhance protection from bacteria, viruses, and other organisms. Because they are not as reactive to organic material in water as chlorine, chloramines produce substantially lower concentrations of disinfection byproducts in the distribution system.[4] "Chloramines are less reactive with organic matter and more persistent—two characteristics that are presently deemed highly desirable in the context of modern disinfection," says Edwards.

According to Edwards, the study proves that water alone can be the cause of pinhole leaks. "Our experiments used copper tube as purchased, as well as copper tube that had been polished to a mirror-like finish to remove all surface contaminants," he says. The composition of the water used in the laboratory was based on the makeup of treated water Edwards and his colleagues collected from areas that were experiencing pitting problems. "[The chlorine and aluminum levels] were only 25 to 50% higher than measured directly in field testing," explains Edwards. "Given the fact that outbreaks of pitting have occurred in many areas when this combination of water factors is present, we strongly feel these factors were already strongly implicated based on the sampling data—even before they were proven with certainty in the lab."

Edwards adds that it is important to consider

This photo shows a MIC-induced through-wall pit in copper pipe on a solar panel. Photo courtesy of Paula Scott, CARIAD Consultants, Heraklion, Greece.

the elements that were not included in the tests. "Other factors thought by some to cause pitting—including flux, joints, poor plumbing practice, electrical grounding, or lightning—were not present," he says. "Simply exposing the tube to the water in question caused the eight leaks per foot in 1 year. The surface that had been polished to a mirror-like finish was also severely pitted. We had only two factors: the water and the pipe. There is no other explanation."

The Aluminum Anomaly

Andrew J. Kireta, Jr., CDA's National Program Manager for Tube, Pipe, and Fittings, contends that Edwards' conclusion is significant for two reasons. "This finding stresses the importance of considering the impact of water treatment and water chemistry changes and regulations on the distribution systems and materials," he says. Kireta finds equally important Edwards' observation that the aluminum in the water plays a significant role in the pinhole leaks. "Aluminum could be considered the major contributing factor in this situation because it is the anomaly," he says.

"Chlorine, which exists in some level in virtually all publicly delivered water supplies in the U.S., was shown not to cause the corrosion concern on its own," says Kireta. "Only in the presence of aluminum did the pinhole leaks develop. This is significant because, while aluminum is present in many treated waters at low levels, never before was it found in significant levels where pinhole leaks had occurred in cold water systems." In fact, Kireta says that CDA's copper tubing research only began to show significant levels of aluminum on corrosion pits and in water deposits on a regular basis in the late 1990s. "Before this time, aluminum was rarely detected," he says. "This indicates that changes being made to water chemistry are causing an increase in the amount of aluminum delivered to the home water distribution system, either through aluminum being added to the treated water or, more likely, the leaching of aluminum from the public water distribution system."

Kireta believes that the study is ground-breaking because it finally provides the evidence explaining why "epidemics" of corrosion are occurring in domestic water systems in the District of Columbia and elsewhere in the U.S. "Prior to this work, it was commonly assumed that the only link between corrosion outbreaks in different utilities was the fact that copper tube was involved and suffering pinhole leaks," he says. "This would inevitably lead to what has now been proven to be a mistaken conclusion that the problem was due to faulty or inferior copper tube or a result of something in the manufacturing process that made the tube unsuitable for use. This work proved beyond a shadow of a doubt that the only significant factor in causing the corrosion was the chemistry of the water—and that the copper tube surfaces were not the cause of the failures."

What About MIC?

Another known cause of pitting in copper tubing is MIC. The inherent toxicity of copper ions initially led some to assume that copper alloys could ward off MIC. However, copper-tolerant strains of bacteria now are known to exist. "The mechanisms of corrosion by bacteria are numerous," says Paula Scott, Principal of CARIAD Consultants (Heraklion, Greece) and an internationally recognized expert on biological corrosion. "They differ in copper only in that, since copper is naturally microbiocidal, bacteria protect themselves by typically producing copious amounts of a gelatinous goo called 'extracellular polymeric substances.'"

Scott notes that MIC can occur wherever bacteria are present. Like all living organisms, bacteria need free water to survive. They also typically live in temperatures below 176°F (80°C), but Scott points out that that some thermophilic bacteria can endure higher temperatures. Chlorine and other biocides most often are used to control MIC.

"The more we look, the more we find it," says Scott of MIC-induced pitting in copper tubing. "MIC of copper has been found in several countries so far and is probably more widespread than we think, especially where water treatment is inadequate." Nevertheless, copper pitting is still con-

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The Lead and Copper Connection

Some ascribe the unusually high number of copper pitting cases in suburban Washington, D.C., and elsewhere to the water chemistry required by the EPA's LCR. Could the treatment practices mandated by the rule also attack other metallic components of plumbing and cause lead to leach from residential service lines into drinking water?

In recent months, the detection of high levels of lead in tap water supplied to older Washington, D.C., residences has received considerable public scrutiny. The LCR requires a water system to use certain treatment techniques when samples reach an EPA-defined "action level" of 15 ppb of lead. The EPA, which is responsible for ensuring the safety of drinking water in the District of Columbia, received a report in July 2001 from the District of Columbia Water and Sewer Authority (WASA) showing elevated concentrations of lead in water samples taken from residences in the WASA service area. A subsequent report, for the period July 1, 2001, to June 30, 2002, revealed that lead levels exceeded the action level in 26 of the 53 samples taken for that monitoring period. A test conducted in the summer of 2003 revealed that two-thirds of 6,188 District homes had water that exceeded the lead action level. Moreover, WASA found that more than 150 of these homes had lead levels exceeding 300 ppb—more than 20 times EPA's action level. It has been reported that a few samples even had lead levels in the thousands of parts per billion, exceeding thresholds for hazardous waste. Because an estimated 23,000 homes in the city utilize lead service lines, some believe that the number of "exceedances" is much greater. At this writing, however, approximately three-fourths of the homes have not been tested—nearly 3 years after the first reports of elevated lead levels. Moreover, the matter did not begin receiving widespread publicity until early this year when it was the subject of a *Washington Post* article.[8]

Aggressive water can attack metallic plumbing materials other than copper. Exceedances of the EPA's lead action limit can force utilities to replace existing lead pipe. This photo shows a pit dug to partly replace an existing publicly owned lead pipe with a copper pipe. Photo courtesy of Marc Edwards, Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia.

What is causing this rapid increase in lead exceedances? No conclusive answer was available at press time. However, it is clear that the corrosivity of the District's drinking water increased when the U.S. Army Corps of Engineers in November 2000 switched to chloramines (from free chlorine) as a secondary disinfection agent at the Washington Aqueduct. Testifying at a recent congressional oversight hearing, Washington Aqueduct General Manager Thomas P. Jacobus stated that the disinfection practices were modified in order to comply with EPA regulations.[9]

In an EPA-commissioned study and in his testimony to Congress, Edwards reported that in some circumstances chloramines dramatically increased lead leaching to water from pure lead pipe or leaded brass. Edwards' report, submitted to the EPA in October 2003, also suggests that introducing orthophosphates or other phosphate-based corrosion inhibitors could stop the leaching.

The detected and undetected instances of lead leaching notwithstanding, the turn of events in Washington, D.C., has generated a separate controversy among various government officials. D.C. city leaders as well as members of Congress have criticized WASA and the D.C. Department of Health for responding slowly to the crisis. The agencies have since begun distributing water filters to homes with lead service lines. EPA officials also have charged WASA with violating federal law. In addition, the chairman of the U.S. House subcommittee that has prime jurisdiction over the Safe Drinking Water Act recently asked the General Accounting Office (GAO) (Washington, D.C.) to conduct an independent inquiry into the operation of WASA and the Washington Aqueduct and the manner in which the public was notified about test results showing elevated lead levels. "My prime concern is that the public health is protected," U.S. Representative Paul Gillmor (R-Ohio), Chairman of the House Energy and Commerce Subcommittee on Environment and Hazardous Materials, noted in a written statement. "We need to gather all the information before making any final decisions or conclusions, but with some of D.C.'s lead levels approaching 20 times the safe limit set by the EPA, I am inclined to believe this was not so much a failure of law, but of persons."

For updates on this ongoing story, access the following Web sites:

- D.C. WASA: www.dcwasa.com
- D.C. Department of Health: dchealth.dc.gov/index.asp
- U.S. EPA Region 3: www.epa.gov/region3
- U.S. House Committee on Government Reform: reform.house.gov/GovReform/Hearings/EventSingle.aspx?EventID=797
- U.S. House Energy and Commerce Subcommittee on Environment and Hazardous Materials: energycommerce.house.gov/108/subcommittees/Environment_and_Hazardous_Materials.htm.

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sidered a rare phenomenon in industrialized countries.[5] Furthermore, it is important to remember that more advanced water treatment systems do have a built-in defense against MIC. "One of the reasons that piping is not corroded more in potable water systems is that in most places, water treated for human consumption is pretty well free of bacteria," says Scott. She does point out, however, that what is considered "potable" in one locale may not be so in another. "It would be very naive to think that all potable waters are adequately treated around the world," she says.

Acknowledging his own research that sulfate-reducing bacteria can likely cause copper pitting corrosion, Edwards echoes Scott's point that potable water is not typically an ideal place for MIC-causing bacteria to flourish. "If you look at many previous studies examining MIC, the researchers almost always utilized nutrient media that are highly unrepresentative of drinking water," he says. "For instance, it is not uncommon for MIC researchers to use levels of orthophosphate [as a nutrient source or buffer], grams per liter of organic matter such as glucose [$C_6H_{12}O_6$], and even grams per liter concentrations of ammonia in MIC experiments. In such cases, the 'water' is more representative of concentrated raw sewage than drinking water, and I strongly argue that results from such studies cannot be readily extrapolated to potable water systems. The fact of the matter is that despite years of study, MIC corrosion has never been proven to cause fully penetrating copper pitting as it occurs in real systems. In drinking water systems, addition of even 1 mg/L orthophosphate completely alters copper corrosion, 0.1 mg/L of biodegradable organic matter is a concern for bacteria regrowth, and ammonia concentrations rarely exceed a few milligrams per liter."

Contrasting the above MIC research scenario with his own copper pitting study, Edwards says that he and his colleagues limited bacterial activity with a relatively high pH of 9.2, continuous high free chlorine disinfectant residuals (greater than 3 mg/L), and the omission of any added organic matter, NH_3, or phosphate. "Not surprisingly, measurements of bacterial activity were negligible," he says. "Yet extreme pitting did occur."

Scott points out that MIC corrosion indeed has been shown to cause fully penetrating copper pitting in actual water systems. In a NACE International book that she recently coauthored with Michael Davies, her partner at CARIAD, Scott cites instances in which MIC caused through-wall pitting in real systems.[6] "That doesn't mean it is the cause in all cases, but it certainly is in some," she says. "There is room for more than one mechanism of corrosion in copper tubing. Probably, some corrosion mechanisms, not involving bacteria, operate at high biocide levels. MIC operates…in systems where the water treatment is inadequate."

Scott also notes that carbon dioxide (CO_2) contributes to copper pitting in cold potable water. It has been stated that dissolved CO_2 in aggressive water initiates pits and depolarizes the cathodes on the copper when the metal is exposed to cold water.[7] Space limitations preclude a more detailed discussion of the role of CO_2 in copper pitting in this article.

Not the Last Word?

Edwards points out that the level of scientific understanding of copper pitting remains very limited, and he dispels any inference that the Virginia Tech study presents the sole explanation for the phenomenon. "I believe it is likely that there are other situations that will create aggressive water that can eat holes in a copper pipe, and with further testing we can identify those that are most important and how to prevent them" he says. "It is important to note that pitting can be mitigated by either preventing production of aggressive water in the first place or by addition of corrosion inhibitor."

According to Edwards, his own 12 years of study into "most of the other purported causes" never found that these factors cause pitting by themselves. "This does not mean that someone might someday do the test slightly differently and prove they do cause pitting," he concludes. "But the onus is now on others to develop that proof, because our team has now shown that it can be caused by the water alone."

References

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9. House Committee on Government Reform, The Federal Role in Ensuring Safe Drinking Water in the District of Columbia: Oversight Hearing, 108th Cong., 2nd sess., 2004. MP