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Evaluation of Corrosion of Copper Drinking Water Pipes Exposed to Sulfurous Well Water and Ozone Treatment

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ABSTRACT

Copper pipes used in a home plumbing system experienced repeated pinhole leaks. These leaks occurred approximately nine years after the home was occupied, and eleven years after construction of the home. The home is supplied by a private well with sulfurous water. To ameliorate the unpleasant effects (taste and odor) of the sulfurous water, an ozone treatment system was installed seven years after occupation of the home. During the intervening period following the treatment system installation, multiple pinhole failures became evident. Upon examination of pipes removed during repair, a thick layer of dark green and black corrosion products was observed on the interior, with areas of pitting observed up to several centimeters in length. This paper will describe the composition and morphology of the deposits formed inside the copper pipes, pitting corrosion observed and the potential effects of the combination of sulfurous water and ozone treatment on the localized corrosion of the pipes.

Key words: copper pipes, ozone, drinking water, well water

INTRODUCTION

A privately owned home in the western United States has drinking water supplied from a private well. The water is supplied to and throughout the house with copper pipes. The as-supplied water is considered by the occupants to have an objectionable sulfurous taste and odor. To reduce the unpleasant effect of the sulfur in the water, an ozone generator was placed in the supply line. The ozone generator is located in the yard, downstream of the well, and about seventy-five feet (23 m) upstream of, a proprietary sulfide removal filter and water softener, located in the garage. The water is distributed throughout the home, after the sulfide filter and softener.

Pinhole leaks were detected in the copper piping running from the ozone generator to the filters, and within the piping in the home. Piping samples were examined to determine the mechanism of corrosion.

After the first instance of leakage, it was suspected that ozonation of the water may be contributing to the pinhole corrosion. For this reason, the ozone generator was turned off. The sulfide filter and water softener remained online.

Approximately one and one-half years after the initial leak, another pinhole leak was discovered. This pipe was inside the home, and therefore downstream of the sulfide filter and water softener. Another pipe segment was also removed from the line downstream of the ozone generator, but upstream of the filter and softener.

Two years after the initial leak, pipe samples that did not exhibit leaks were removed from the line immediately upstream and downstream of the filters and softener in the garage to further evaluate the effects of the varying water chemistry on pipes.

All the submitted pipe samples were examined visually, microscopically and chemically to evaluate degree of pitting, as well as characterize and determine the composition of the corrosion products. The goal of the evaluation was to determine if the water chemistry and the chemical composition of the corrosion products was related to the degree of pitting observed in the copper pipes. In addition, water samples supplied were characterized to further understand contribution of water chemistry to the corrosion reactions.

LITERATURE REVIEW

Published literature was reviewed regarding the effects of sulfurous water and ozone treatment of water, on copper pipes. No literature was found identifying or describing the presence of sulfide in the water in combination with an ozone treatment. Therefore, the review provided here summarizes the two effects independently.

Effect of sulfide on copper pipes

Well waters containing hydrogen sulfide have been associated with pitting attack of copper pipes. The corrosion products were indicated to be Cu_2O (cuprite), copper sulfate and copper sulfides. The author indicates that hydrogen sulfide can be removed by aeration in a forced-draft tower, indicating that oxidation of the sulfide is an effective removal technique.¹

Studies of the effect of exposure of copper pipe samples to simulated tap water with and without sulfide addition at two pH levels (6.5 and 9.2) indicated substantial increases in corrosion rate with the presence of sulfide, with the greatest increase at pH 9.2.² These previously exposed samples were subsequently exposed to simulated tap water without sulfide, and the corrosion rate increased by approximately an order of magnitude compared to that of similar copper tubes that were never exposed to sulfide. Further studies indicated that the sulfide scale present on the copper catalyzed corrosion of the copper, even when water chemistry was changed. Also, deaeration of the water did not lead to a reduced corrosion rate where a sulfide scale was pre-existing.²

A similar study evaluated the effect of mitigation strategies on the corrosion rate of copper exposed to simulated tap water with sulfide; ozonation was not among the strategies considered.³ Removal of soluble sulfides from the water stream did not have a substantial effect on the corrosion rate of the copper with preexisting sulfide films. Chlorination with sodium hypochlorite led to an increase in corrosion rates. Deaeration did not lead to reduced corrosion rates; however, the authors concluded that aeration could lead to increased corrosion rate but did not elaborate on this.³

Effect of ozone of copper pipes

A study on the effect of ozonation and biofiltration on copper corrosion, particularly with respect to alteration of total organic carbon concentrations and specific chemical species was reviewed. Ozonation of lake water was found to increase the concentration of dissolved copper and the corrosion rate. This increase was linked to changes in chemical species (particularly the formation of acids) as a result of the ozonation of the organic molecules in the water stream, rather than direct attack of ozone on the copper pipe.⁴

Another study evaluated the effects of ozonation of deionized water on the corrosion rate of copper. In this study, in ultrapure water (absent other compounds that are present in drinking water), ozonation substantially increased the corrosion rate in both stagnant and flowing conditions, implying that ozone can have a direct effect on copper, rather than just on the components of the water stream.⁵

Effect of pH, chloride, sulfate and alkalinity on copper pipes

There is much literature published on pitting and uniform corrosion of copper drinking water pipes. While the literature is not in complete agreement, cold water pitting is often considered to be associated with tap water with high sulfate to chloride, or sulfate to bicarbonate ratios.^{6,7,8,9} The pH range of these waters is typically in the 7.0 to 7.8 range. Note that these studies do not involve water with sulfide or ozone present.

Reaction Between Hydrogen Sulfide and Ozone

In groundwater sources, sulfur exists predominately as H₂S and HS⁻ in the pH range of 6-8.¹⁰ The oxidation reaction of hydrogen sulfide by ozone is considered to be summarized by Equation 1, although reaction mechanism and kinetic studies have typically been performed in the gas phase, rather than liquid water.¹¹



Reaction rates, of course, depend on a number of factors, including concentrations of reactants, temperature, and other chemicals present in the water that may also react with the reactants, but the hydrogen sulfide concentrations can be reduced by approximately 37 percent in 60 seconds.¹¹

EXPERIMENTAL PROCEDURE

Pipe Samples

Five pipe samples were provided for laboratory evaluation over the course of two years. Of these, all five samples are downstream of the ozone generator, and two pipes are additionally downstream of the sulfide filter and water softener. A summary of the samples with brief descriptions is shown in Table 1.

Pipe samples were removed and provided to the laboratory for analysis. After initial evaluation, pipes were cut lengthwise to expose the interior surfaces using a bandsaw without lubricant to limit contamination of the cut surfaces. Cut samples were examined visually and using a stereomicroscope. Selected areas were selected for preparation of polished cross-sections for further microscopical examination and analysis by scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDS). SEM/EDS analyses were carried out using a JEOL 6010 LA SEM[†] operated at 20kV, in both high vacuum and low vacuum (30 Pa) conditions. Images were collected in backscatter mode. Corrosion products were removed from the pipe interior surfaces with a steel implement and analyzed using x-ray diffraction (XRD). XRD analyses were conducted on a Bruker D8 Advance[†] diffractometer

[†] Trade Name.

using cobalt or copper K α radiation. Composition of the pipe from Sample 1 was measured on an ARL 4460[†] optical emission spectrometer.

Table 1
Investigated Pipe Samples

Sample Designation	When Removed (Years After Occupancy)	Pinhole Present?	Location
Sample 1	9	Yes	Upstream of sulfide filter and water softener, collected while ozone generator was still in operation
Sample 2	10-1/2	Yes	Downstream of sulfide filter and water softener (from inside the home)
Sample 3	10-1/2	No	Downstream of ozone generator
Sample 4	11	No	Immediately upstream of sulfide filter and softener
Sample 5	11	No	Immediately downstream of sulfide filter and softener

Corrosion products were removed from the interior of portions of selected pipe samples using a 50% aqueous hydrochloric acid solution and agitation with a plastic-bristle brush. After removal of the corrosion products, the interior surfaces were further examined visually and microscopically.

Water Samples

Three water samples were provided for laboratory analyses: Tap water (from a faucet in the home), water from the ozone tank, and water from the well tank. Because the testing was performed in the laboratory, sulfide and ozone concentrations could not be measured, as those need to be measured at the time of collection. Concentrations of fluoride, chloride, sulfate, nitrate, nitrite, bromide and phosphate were measured using ion chromatography. Ion chromatography was conducted using a Dionex ICS 2000[†] ion chromatograph with hydroxide eluent and a Thermo-Fisher AS 15[†] column. pH was measured with Thermo Scientific Orion Star A21[†] pH meter. Alkalinity was measured by titration with sulfuric acid.

RESULTS AND DISCUSSION

Visual and Microscopical Examination of Pipes

Sample 1

Sample 1 was received approximately nine years after occupancy of the home. Leakage occurred due to pinhole corrosion originating on the inside surface of the pipe. Multiple layers of corrosion products were apparent on the pipe, with reddish corrosion products inside the pits, and a layer of bright green and blackish corrosion products on top. A loosely adhered layer of blackish corrosion products with pale green on top was also present on top of the other corrosion products, but mostly debonded when the pipe sample was cut lengthwise. Wide and deep pits were apparent on the pipe interior, along with one pinhole, as seen in Figure 1. The pits were lined with reddish corrosion products, while the blackish and green corrosion products appeared to sit on top or to the side of the pits. Examination of a polished cross-section of the pipe indicated that red and green corrosion products were present in the pits, and the red, black and green corrosion products sat on the surface of both the pits and the unpitted pipe (Figure 2). The corrosion products thickness was measured at up to 1000 microns.

[†] Trade Name.

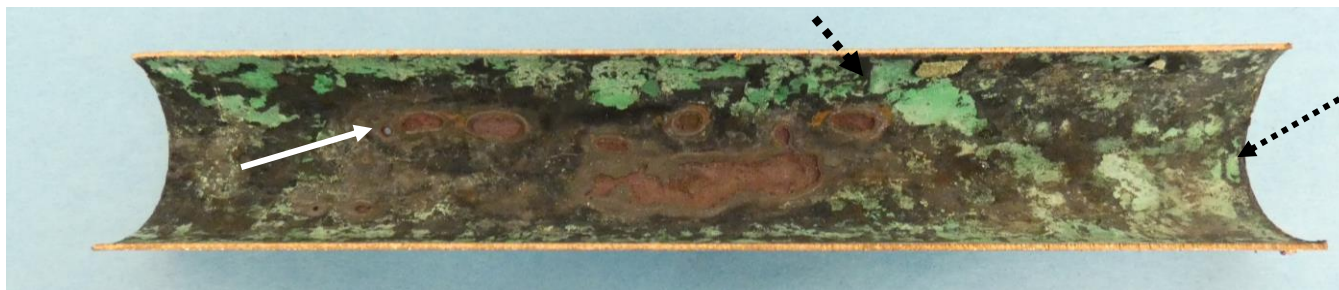


Figure 1: Interior surface of Sample 1, after sectioning lengthwise. The pinhole is indicated with a solid arrow. Remnants of the corrosion products are indicated with dashed arrows.

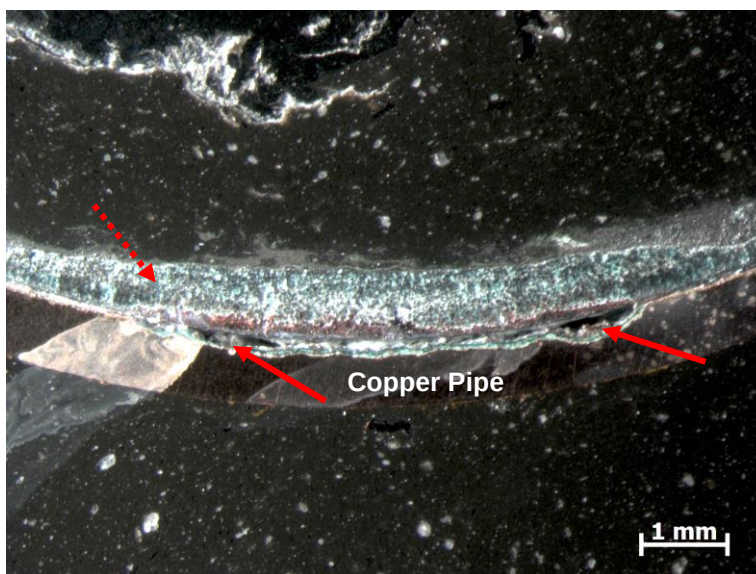


Figure 2: Micrograph of a polished cross-section of Sample 1, taken away from the pinhole. In this location, the thickness of the corrosion products is greater than 1000 microns. Note how the reddish corrosion product sits on and inside the pits (arrows), and the blackish and green corrosion products remain on the surface (dashed arrow).

SEM/EDS analysis of the corrosion products indicated the presence of sulfur associated with the green and black corrosion products (see Figures 3 through 5). Each EDS spectrum in these Figures has a number in the upper left which correlates with the location indicated with cross-hairs in the corresponding micrograph. As discussed above, sulfide in water has been associated with corrosion of copper^{1,2,3}. Areas of silicon-rich deposits were also detected in the pale green corrosion products. Aluminosilicate deposits on the interior of pipes, formed from alum coagulation of dissolved silica have been associated with copper corrosion.¹² While this water stream was not alum-treated, the high levels of silicon detected in the corrosion deposits may be associated with deposits that can affect the corrosion rate.

No markings were apparent on the exterior of Sample 1 or any of the pipes, in part because a thin layer of corrosion product was present. The pipe chemistry was analyzed using optical emission spectrometry and determined to be copper with 0.024% phosphorus, which is consistent with UNS C12200, which is specified for drinking water pipe by ASTM⁽¹⁾ B88.¹³

⁽¹⁾ ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959