Evaluation of Copper Pitting in Cobb County, Georgia

Final Report

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INTRODUCTION

Cobb County-Marietta Water Authority (CCMWA) is a surface water utility in northwest Georgia, operating two water treatment plants (Quarles and Wyckoff) and serving 11 wholesale customers. Raw water is treated with a conventional approach: oxidation, coagulation, flocculation, sedimentation, and filtration. Water is disinfected with sodium hypochlorite and lime is added to raise pH for corrosion control.

The CCMWA distributes relatively low mineral content water that is poised in an appropriate pH range to minimize lead and copper solubility. It is adequately buffered, and contains low levels of chlorides, sulfates and silicates. The CCMWA has been in full compliance with the EPA's Lead and Copper Rule for the past 20 years, meaning that the CCMWA has instituted what the US EPA recognizes as Optimal Corrosion Control Treatment (OCCT). OCCT is designed to minimize both lead and copper corrosion, but also provides corrosion benefits relative to other materials. Lead and copper levels (90th percentile) as reported by the CCMWA are exceptionally low.

Recently customers have been experiencing pinhole leaks, so the objective of this study was to examine whether the problems experienced by CCMWA customers are similar to established causes of pitting corrosion.

MATERIALS AND METHODS

Thirteen copper pipes with pinholes from CCMWA were harvested and shipped to Virginia Tech for forensic analysis (**Table 1**). Each pipe was cut longitudinally so that the interior surfaces could be examined.

Table 1: Identifying information for copper pipe samples from CCMWA.

ID #	Address	House Built / Age of Plumbing	Cold or Hot Water Pipe	Horizontal or Vertical Run
1	Old Alabama Road, Acworth GA 30102	1981	Cold	Horizontal
2	Tritt Springs Circle NE, Marietta GA 30062	1983	Cold	Vertical
3	Pine Road, Marietta GA 30066	1983	Cold	Vertical
4	Meadow Wind Lane, Marietta GA 30062	1987	Cold	Horizontal
5	Wicks Drive, Marietta GA 30062	1978	Cold	Horizontal
6	Woods Field Lane, Marietta GA 30062	1981	Cold	Horizontal
7	Courtney Lane, Dallas GA 30132	1998	Cold	Horizontal
8	Blakeford Way, Marietta GA 30062	1981	Cold	Horizontal
9	Fairhaven Ridge, N.W., Kennesaw GA 30144	1978	Cold	Horizontal
10	#1 Karls Gate Drive, Marietta GA 30068	1978	Cold	Horizontal
11	Clinton Drive, Marietta GA 30062	1998	Cold	Horizontal
12	#2 Karls Gate Drive, Marietta GA 30068	1995	Cold	Horizontal
13	West Carlyle Ct., Marietta GA 30062	1977	Cold	Horizontal

One to two pits on each pipe were selected for a 'spot test' analysis. Since sulfide attack is one established cause for pinholes, the method described by Feigl and Angel (1972) in "Spot Tests in Inorganic Analysis' was utilized. In this method a small drop of a sodium azide-iodine solution is placed on the pit covering one of the pinholes. Any solid metal sulfide present would immediately react and result in the evolution of nitrogen gas, which can be visually detected by the bubbles on the surface of the pit.

One pit from each of ten pipes was removed for analysis by inductively coupled plasma mass spectrometry (ICP-MS) and by electron scanning microscopy with an attached X-ray energy dispersive system (ESEM-EDS). A portion of the pit was weighed and placed in a 125 mL HDPE bottle with 80 mL of deionized distilled water and 20 mL of trace metal grade nitric acid. Bottles were placed in an oven at 70 °C for one day to allow the solid to dissolve. The resultant solutions were diluted 1:10 and analyzed by ICP-MS for metals' concentrations. Another portion of the pit was mounted and analyzed directly by ESEM-EDS for elemental composition (note that the microscope was used to select areas of analysis within each sample).

Two water samples were obtained from the two surface water treatment plants and shipped to Virginia Tech for analysis. Each sample was preserved by acidification with trace metal grade nitric acid (2% v/v) upon arrival at Virginia Tech and allowed to sit at least 24 hours prior to analysis by ICP-MS for metals concentrations.

The thickness of each copper pipe was determined using a set of Mitutoyo calipers.

RESULTS AND DISCUSSION

Representative photographs of the interior and exterior surfaces of each copper pipe are shown in Appendix 1, **Figures A1.1-A1.13**. Each pipe evaluated had non-homogeneous pitting on the interior surfaces and some outer surface corrosion due to water escaping through the pinhole leaks.

The ESEM-EDS analysis of the copper pipe pits showed that sulfur was present in many of the pits analyzed (**Table 2**) as composition ranged from 0 to 8.8 mass percent, with an average of 3.4 mass percent. The primary elemental composition of all pits was about 50% copper and 34% oxygen, on a normalized mass percentage basis. Small amounts of carbon, aluminum, and silicon were also present in most pits.

Table 2: ESEM/EDS data from pit analysis in mass percent.

Sample ID	Element											
	C	O	Mg	Al	Si	P	S	K	Ca	Fe	Cl	Cu
1	2.2	44.6	0.6	5.7	11.5	0.5	0.7	0.3	0.4			33.5
	0.9	42.9	0.5	5.9	10.7	0.7	0.9	0.3	0.5			36.8
	1.8	43.5	0.5	5.5	11.1	0.5	0.7	0.3	0.3			35.7
	1.8	44.0	0.6	5.5	11.5	0.5	0.8	0.3	0.3			34.5
	2.4	46.3	0.6	5.5	11.2	0.5	0.8	0.3	0.3			32.1
	0.4	46.0	0.5	5.8	11.0	0.7	0.7	0.3	0.4			34.2
	2.1	45.9	0.6	5.7	10.9	0.7	0.8	0.3	0.4			32.8
	3.4	21.7		4.1	1.8	0.6	5.4		0.2			62.8
	2.8	21.4		2.5	3.9	0.9	4.5		0.3			63.8
	5.5	19.6		3.5	1.2	0.4	6.2		0.2			63.5
2	5.3	28.4	0.2	0.8	3.9	0.1	0.6					60.6
	6.3	33.2	1.1	0.9	1.3	0.4	1.5			1.0		54.5
	4.3	22.5		0.5	2.0	0.1	0.5			0.5		69.6
	5.1	28.6		0.8	0.3	0.3	4.7					60.2
	7.9	29.1	1.0	1.5	3.3	0.4	0.5					56.4

Table 2: ESEM-EDS data from pit analysis in mass percent (continued).

Sample ID	Element											
	C	O	Mg	Al	Si	P	S	K	Ca	Fe	Cl	Cu
3	6.2	37.6		0.5	3.9		4.6					47.2
	5.8	37.6		0.6	6.2		3.3					46.5
	5.8	35.5		0.9	3.2		4.4					50.2
	1.8	40.1	0.3	0.7	6.9		3.2		0.1			46.9
	1.8	38.0	0.2	0.5	3.7		4.8		0.1			50.9
4	3.8	33.2	1.4	3.7	7.6				0.5	1.0		48.9
	7.0	34.7		4.1	9.4		0.1					44.7
	8.0	25.7		4.6	10.2		0.1					51.4
	5.6	23.6		1.2	5.5	0.2	0.8					63.1
	5.5	29.4		1.0	1.6		3.9					58.5
	7.2	35.1		1.3	2.8		2.4				0.7	50.7
5	6.0	25.2		0.3			3.9					64.7
	9.1	41.3		0.2			4.1					45.3
	6.6	48.1		0.4			5.7					39.3
	13.0	39.8		0.7	8.6		1.5					36.5
	6.4	34.9		0.3	0.8		6.4					51.2
	5.0	34.9		0.3			6.9					53.0
6	4.0	20.7		0.4			8.8					66.2
	4.3	21.0		0.6			8.0					66.2
	11.8	35.6		0.2			5.8					46.7
	7.2	28.7		0.6	1.0	1.1	1.8			1.6		58.1
	5.1	33.3		0.2			6.4			0.1		54.9
	4.5	23.2		0.3		0.2	8.7					63.1
7	7.7	29.0		1.3	1.0		6.0					55.0
	6.6	34.8		0.3			6.7					51.7
	7.7	40.1		1.1			5.8					45.3
	8.6	41.9		0.7	2.6		4.8					41.4
	7.3	39.7		2.0	0.3		5.0					45.8
8	9.5	26.7		1.0	3.2		5.1			0.6		53.7
	8.9	32.7		0.7	1.8		5.9		0.2	0.5		49.3
	7.1	32.3		0.6	1.5		6.3		0.4	0.5		51.4
	7.7	44.5		0.4			6.0					41.5
	7.7	38.7		0.3	0.4		6.1					46.8
9	22.9	34.2		0.6	4.4		0.2					37.6
	7.5	34.8		0.4	0.7		2.0					54.8
	5.2	26.9		1.2	0.1		5.6					61.0
	11.5	35.7		0.4			1.7					50.8
	5.5	33.3		1.2	5.9		0.5					53.6
	5.1	26.9		0.3	7.5							60.3
	6.5	28.6		2.8	6.1		1.2					55.0
	5.6	36.9		2.0	5.6		0.9					49.1
	5.0	30.9		1.0			6.5					56.6
10	3.3	38.2		5.2	12.3				0.6	0.7		39.7
	6.1	42.9		3.5	9.3		0.4		0.5	0.3		37.0
	8.4	30.0		5.1	12.2				1.0	1.4		42.0
	3.8	30.6		5.5	14.4				1.0	1.0		43.7
	2.8	36.9		1.8	8.5		1.5		0.3	0.1		48.2
	11.3	42.7		3.4	9.7		0.1		0.4	0.3		32.2
	9.2	30.8		4.9	11.8		0.1		1.4	1.3		40.5
avg =	*6.1*	*34.0*	*0.6*	*2.0*	*5.7*	*0.5*	*3.4*	*0.3*	*0.4*	*0.7*	*0.7*	*49.7*
max =	*22.9*	*48.1*	*1.4*	*5.9*	*14.4*	*1.1*	*8.8*	*0.3*	*1.4*	*1.6*	*0.7*	*69.6*
min =	*0.4*	*19.6*	*0.0*	*0.2*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*32.1*

Note: blank cell indicates element not detected. Carbon=C, Oxygen=O, Magnesium=Mg, Aluminum=Al, Silicon=Si, Phosphorus=P, Sulfur=S, Potassium=K, Calcium=Ca, Iron=Fe, Chloride=Cl, Copper=Cu.

Data from the ICP-MS analysis (**Table 3**) of the pits gave similar results to the ESEM-EDS data. It should be noted that not all the mass was recovered due to limitations of the ICP-MS; that is, ICP-MS is not able to measure elements such as oxygen or carbon. Three pits (6, 7, and 9) were fairly small (weights less than 8 mg) and resulted in recoveries greater than 100% (probably due to larger errors involved with the small weights and the sample dilutions). Data from these pits are not included in the averages listed in Table 3. Similar to the ESEM-EDS small amounts of aluminum and silicon were detected in some pits.

Table 3: ICP-MS data from pit analysis in mass percent.

Sample ID	Mass (mg)	Al	Si	P	S	Cu	Total Mass Recovered
1	23.1	2.3%	1.0%	0.8%	11.9%	52.5%	69.3%
2	13.5				17.9%	51.2%	69.6%
3	13.1		0.9%		19.6%	58.7%	79.8%
4	27.6		0.6%		20.9%	62.5%	84.5%
5	14.8				20.5%	53.7%	74.8%
6	*3.9*				*43.1%*	*68.4%*	*112.0%*
7	*7.7*	*0.5%*			*37.9%*	*88.5%*	*127.4%*
8	16				21.9%	60.4%	83.0%
9	*4.4*	*1.1%*	*1.0%*		*50.3%*	*139.6%*	*192.4%*
10	9.3				24.2%	61.0%	85.9%
avg =					***19.5%***	***57.1%***	***78.1%***
max =					***24.2%***	***62.5%***	***85.9%***
min =					***11.9%***	***51.2%***	***69.3%***

Note: grayed out samples not included in statistics due to large error in recoveries

Results of the ICP-MS analysis of the CCWMA treated water (**Table 4**) show, not surprisingly, that the same elements present in the pit material are present in the bulk water.

Table 4: ICP-MS data for CCWMA treatment plant finished water samples.

Water Treatment Plant	Na (mg/L)	Mg (mg/L)	Al (ug/L)	Si (mg/L)	S (mg/L)	Cl (mg/L)	K (mg/L)	Ca (mg/L)
Wyckoff	8.8	2.1	22.8	3.6	12.3	11.2	2.0	8.6
Quarles	12.6	2.8	21.2	2.5	13.0	14.5	3.3	8.7

Copper pipe wall thickness measurements fell within the normal range for Type M copper (**Table 5**). The 5 readings for each pipe ranged between 80-112% of the specification. Hence the tube was not defectively thin.

Table 5: Wall thickness measurement summary.

Sample ID	Nominal Diameter (in)	Wall thickness (mm)							% avg thk / spec thk
		1	2	3	4	5	Avg	Specification	
1	0.75	0.79	0.84	0.83	0.81	0.85	0.82	0.8128	101.4%
2	0.75	0.84	0.85	0.90	0.89	0.92	0.88	0.8128	108.3%
3	0.5	0.68	0.72	0.72	0.71	0.74	0.71	0.7112	100.4%
4	0.75	0.88	0.92	0.92	0.89	0.92	0.91	0.8128	111.5%
5	0.75	0.78	0.76	0.89	0.78	0.80	0.80	0.8128	98.7%
6	0.75	0.84	0.80	0.81	0.81	0.84	0.82	0.8128	100.9%
7	0.75	0.76	0.77	0.72	0.76	0.75	0.75	0.8128	92.5%
8	0.75	0.82	0.82	0.84	0.82	0.81	0.82	0.8128	101.1%
9	0.75	0.79	0.79	0.90	0.83	0.80	0.82	0.8128	101.1%
10	0.75	0.83	0.87	0.86	0.86	0.82	0.85	0.8128	104.3%
11	0.75	0.64	0.63	0.65	0.64	0.69	0.65	0.8128	80.0%
12	0.75	0.83	0.89	0.86	0.90	0.93	0.88	0.8128	108.5%
13	0.75	0.80	0.82	0.82	0.81	0.80	0.81	0.8128	99.7%

The sulfide ‘spot test’ on selected pits was positive in at least 3 instances. The spot test was also utilized on sodium sulfide to confirm that bubbles were created.

FUTURE WORK

The typical pattern of failure for this type of attack in a distribution system, is that sulfide caused pinholes will be more likely in parts of the distribution system with relatively low levels of chlorine residuals or in homes with relatively low water use. Both of these factors are believed to increase the likelihood of sulfate reducing bacteria growth, which in turn produce sulfides.

Studies should be conducted to document chlorine residuals throughout the system, to determine whether there is increased incidence of sulfate reducing bacteria (SRB) or pinhole leaks, in areas with lower chlorine.

COBB COUNTY-MARIETTA WATER AUTHORITY RESPONSE

In response to Virginia Polytechnic Institute and State University’s recommendation to test for sulfate reducing bacteria, two rounds of tests were conducted. Three sites were tested for sulfate reducing bacteria as follows:

- Courtney Lane, Dallas GA 30132 (known pinhole leaks at residence)
- Pine Road, Marietta GA 30066 (known pinhole leaks at residence)
- Laurel Green Court, Kennesaw GA 30144 (copper pipe, no known pinhole leaks)

In two rounds of testing for the presence of sulfate reducing bacteria, no evidence of such bacteria was found. Below are tables summarizing sample results conducted in March 2018:

Pine Road, Marietta GA 30066	SRB Determination	**Total Coliform**	**HPC MPN**	Free Chlorine
Kitchen	absent	absent	<2	0.16
Spare Bath	absent	absent	48	0.01
Master Bath	SRB **absent** with indication of anerobic bacteria **present**	absent	8	0.95

Laurel Green Court, Kennesaw GA 30144	SRB Determination	**Total Coliform**	**HPC MPN**	Free Chlorine
Kitchen	absent	absent	<2	0.96
Spare Bath	absent	absent	40	0.15
Master Bath	absent	absent	<2	0.72

Courtney Lane, Dallas GA 30132	SRB Determination	**Total Coliform**	**HPC MPN**	Free Chlorine
Kitchen	absent	absent	2	0.74
Spare Bath	absent	absent	62	0.17
Master Bath	absent	absent	30	0.91

Key: Heterotrophic Plate Count (HPC)
Most Probable Number (MPN)

The majority of reported pinhole leaks have come from residences in east Cobb County. In April 2018, four hundred seventy eight (478) free chlorine readings were taken across Cobb County and Paulding County. In east Cobb County along Johnson Ferry Road, Roswell Road and Sandy Plains Road, free chlorine readings ranged from .63 ppm to 1.94 ppm with an average of 1.16 ppm on Roswell Road, 1.46 ppm on Johnson Ferry Road and 1.18 ppm on Sandy Plains Road. Out of 478 samples tested across Cobb and Paulding Counties, free chlorine averaged 1.27 ppm.

Although relatively low chlorine residuals were found in certain plumbing fixtures within the homes tested for sulfate reducing bacteria, free chlorine provided by the Cobb County-Marietta Water Authority in its transmission pipelines and by Cobb County Water System in its distribution pipelines are not low in free chlorine. Infrequent use of plumbing fixtures within homes will result in low free chlorine levels as the water sits stagnant in the home’s pipes.

REFERENCES

Edwards, M., J.F. Ferguson and S. Reiber. The Pitting Corrosion of Copper. ***JAWWA***. V. 86, No. 7, 74-90 (1994).

Feigl, F., and V. Anger. **Spot Tests in Inorganic Analysis**. Sixth Edition. New York: Elsevier Publishing Company (1972).

APPENDIX 1: Photographs of Copper Pipes – Interior and Exterior Surfaces

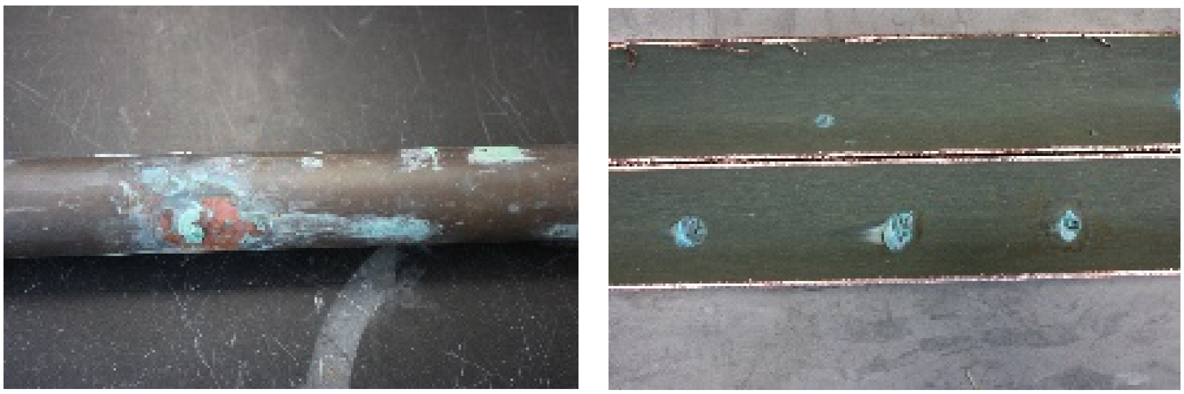

Figure A.1 – Sample #1 exterior (left) and interior surface (right)

Figure A.2 – Pipe #2 exterior (left) and interior surface (right)

Figure A.3 – Pipe #3 exterior (left) and interior surface (right)

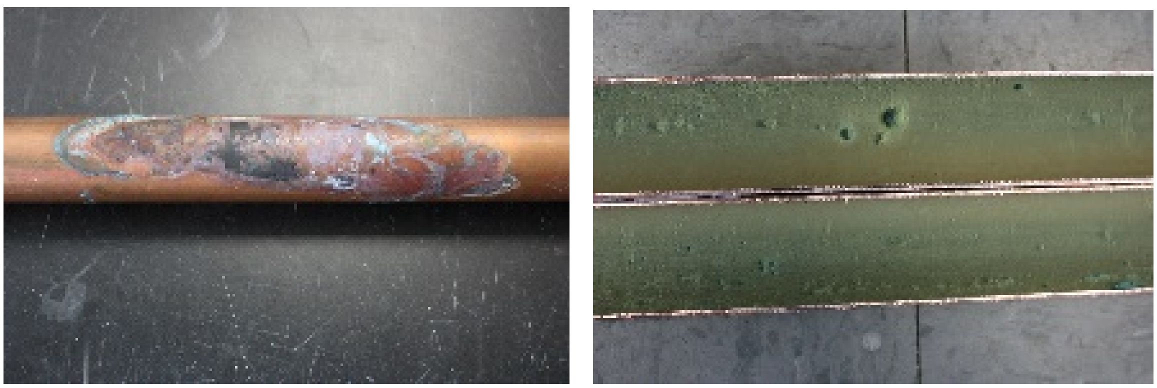

Figure A.4 – Pipe #4 exterior (left) and interior surface (right)

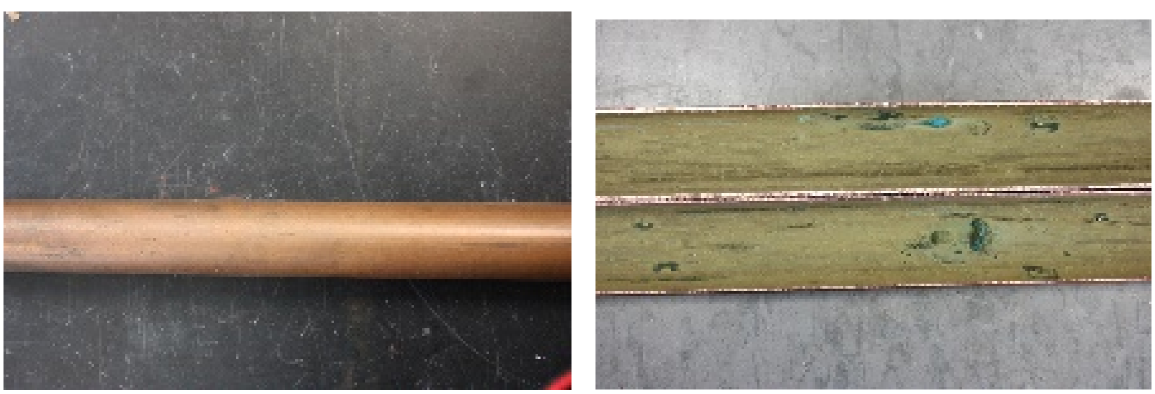

Figure A.5 – Pipe #5 exterior (left) and interior surface (right)

Figure A.6 – Pipe #6 exterior (left) and interior surface (right)

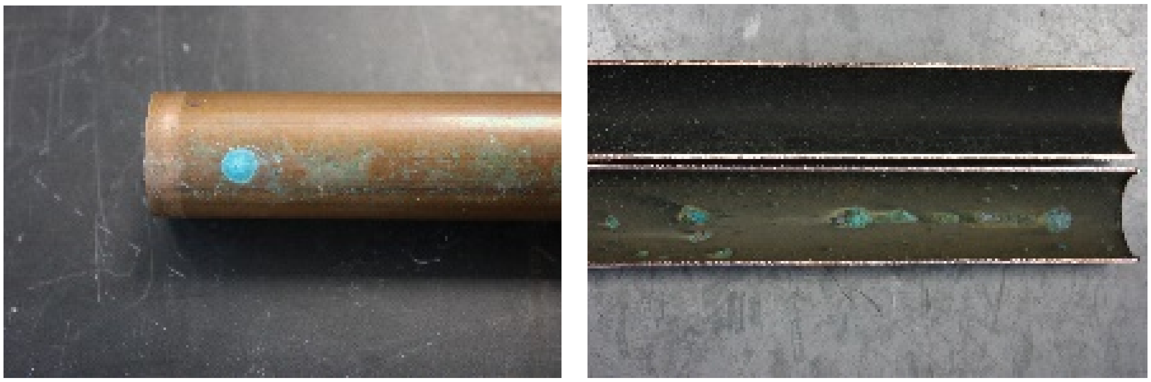

Figure A.7 – Pipe #7 exterior (left) and interior surface (right)

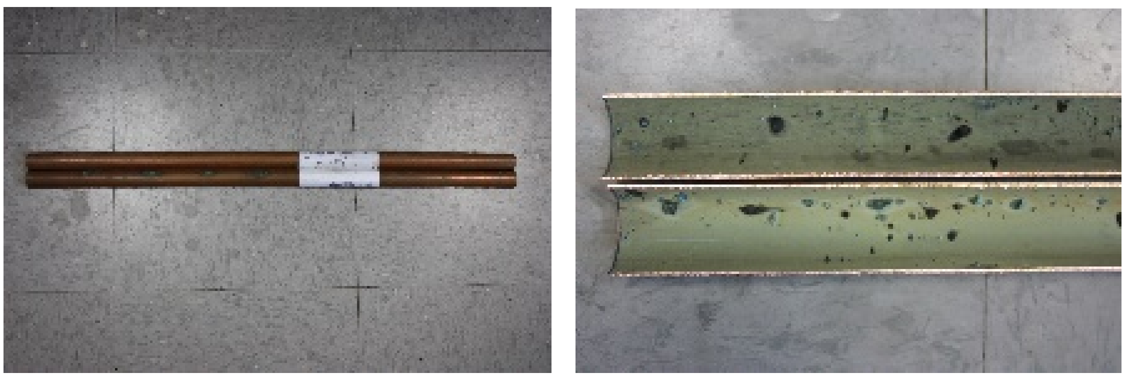

Figure A.8 – Pipe #8 exterior (left) and interior surface (right)

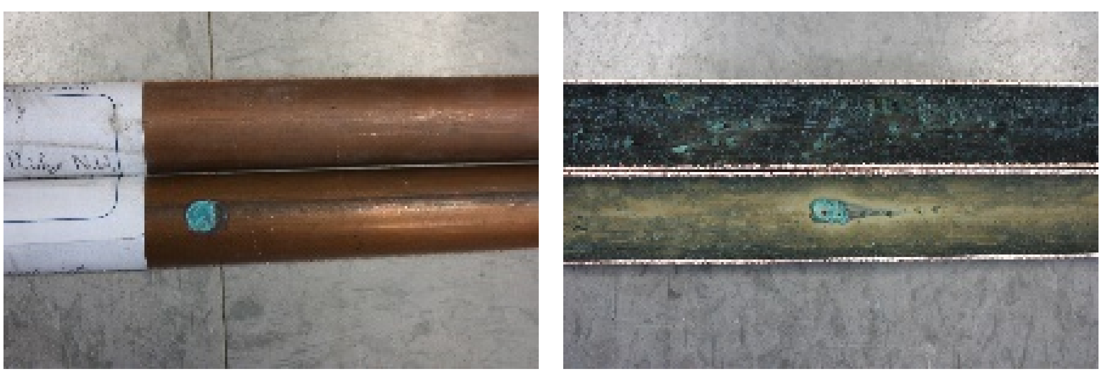

Figure A.9 – Pipe #9 exterior (left) and interior surface (right)

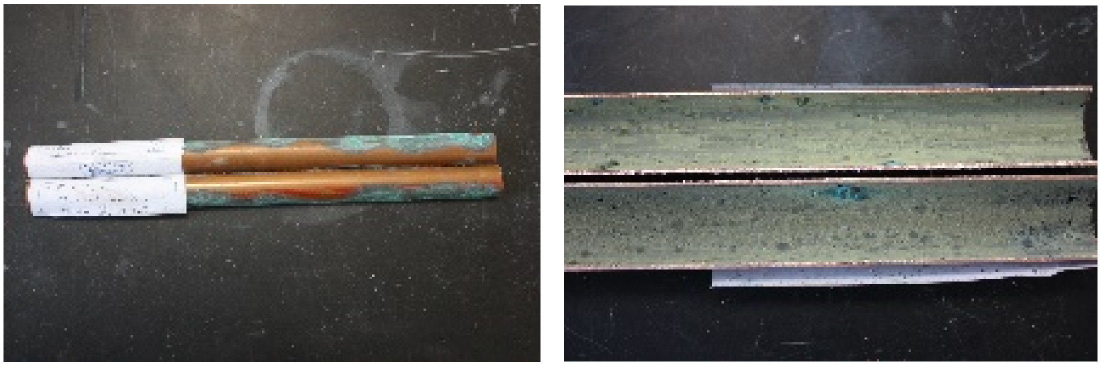

Figure A.10 – Pipe #10 exterior (left) and interior surface (right)

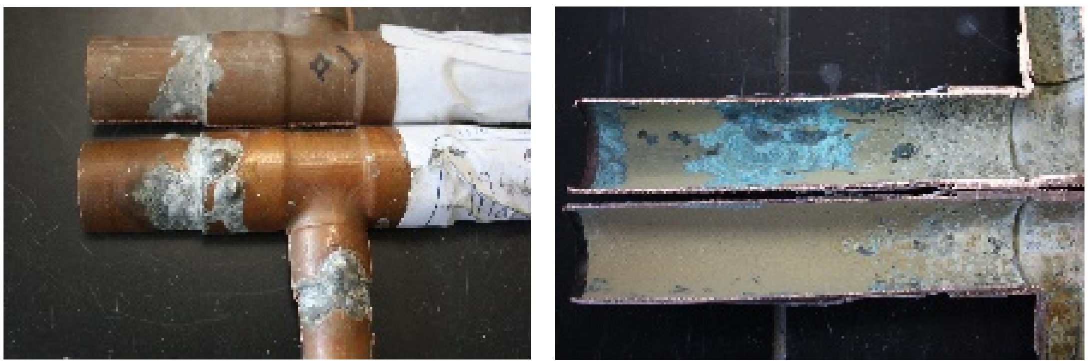

Figure A.11 – Pipe #11 exterior (left) and interior surface (right)

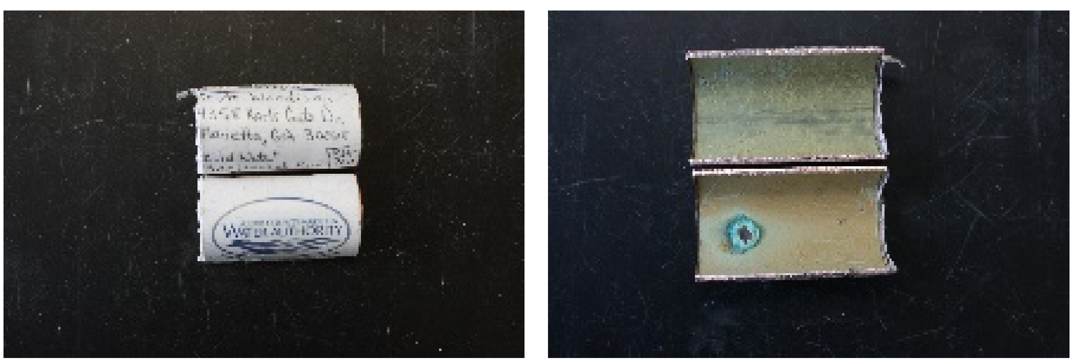

Figure A.12 – Pipe #12 exterior (left) and interior surface (right)

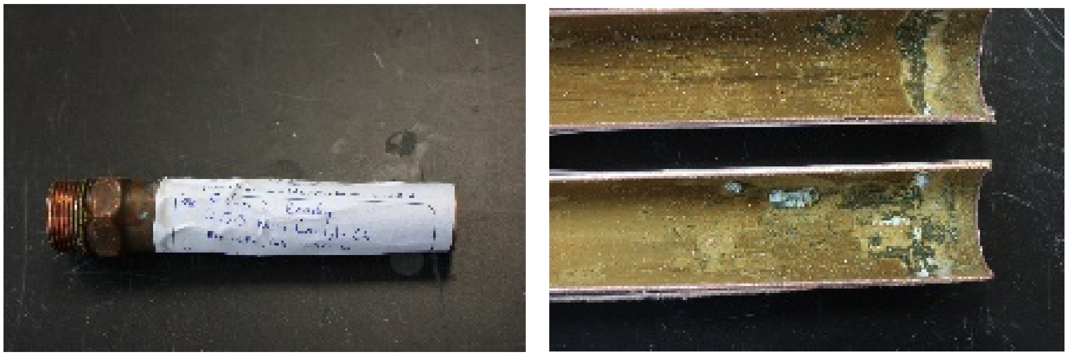

Figure A.13 – Pipe #13 exterior (left) and interior surface (right)