Evaluation of Copper Pitting in Plainview New York

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INTRODUCTION

Plainview (NY) Water District is a groundwater utility on Long Island in New York State. Source water is pumped from 12 wells and lime is added to raise the pH to reduce corrosion. This water is also disinfected with free chlorine, with a typical 0.7-1.0 mg/L as Cl_2 residual level in the system. The water has a very low alkalinity (<10 mg/L as $CaCO_3$) and also contains a moderate to high level of nitrate. Certain wells are also treated for volatile organic compounds by carbon adsorption, while others are treated by air-stripping. Recently customers have been experiencing pinhole leaks in their hot water copper plumbing systems. In particular, hot water pitting is mostly occurring in the 10 feet of pipe after the water heater. The objective of this study was to examine whether the problems experienced by Plainview customers are similar to established causes of hot water pitting corrosion.

MATERIALS AND METHODS

Several copper pipes with pinholes from Plainview, were harvested and shipped to Virginia Tech for forensic analysis. Five representative pipes were selected and cut longitudinally so that the interior surfaces could be examined.

Several pits were selected for a 'spot test' analysis. Since sulfide attack was one possible established cause for the pinholes, the method described by Feigl et al. 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 the 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.

Twelve water samples were obtained from several of the source water wells and ten water samples were obtained from local businesses 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 primary objective behind this testing was to evaluate phosphorus (phosphate) 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 five copper pipes are shown in Appendix 1, **Figures A1.1-A1.5**. 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 sulfide ‘spot test’ on several of the pits in Pipe #1 did not show any evidence of sulfide.

Likewise, the ESEM-EDS analysis of the copper pipe pits showed little sulfide (**Table 1**). Table 1 shows the data in mass percent (top half of Table 1) and in mole percent (bottom half of Table 1). The primary elemental composition of all pits was about 60% copper and 30% oxygen, by mass, or 30% copper and 50% oxygen by mole. A fair amount of carbon was also present in most pits (3-15% by mole). These data suggest that the primary scale formed over these pits was copper oxide or copper carbonate.

Table 1: Summary of ESEM-EDS Data from Pit Analysis

Pipe ID	C	O	Mg	Al	Si	S	Cl	Ca	Fe	Cu
mass %										
NY-1/1	6.0	25.5		1.9	1.7	3.8				64.2
NY-1/2	5.8	33.4		1.6	0.9	3.5	0.8			54.3
NY-2	4.4	22.2		2.5	0.7	3.6	1.3			66.4
NY-3	1.2	33.3		5.5	3.9	1.5		0.5	3.0	51.1
NY-4	4.3	26.6	1.1	3.9	5.0	0.7		0.7	0.5	59.2
NY-5	5.2	24.3		4.3	6.2	1.2				59.6
mole %										
NY-1/1	14.9	47.5		2.1	1.8	3.6				30.1
NY-1/2	13.3	57.2		1.6	0.9	3.0	0.6			23.4
NY-2	12.0	45.2		3.0	0.8	3.7	1.2			34.0
NY-3	3.0	60.5		5.9	4.0	1.3		0.4	1.6	23.3
NY-4	10.6	49.4	1.4	4.3	5.2	0.7		0.5	0.3	27.7
NY-5	13.0	46.0		4.9	6.7	1.1				28.4

Data from the ICP-MS analysis (**Table 2**) indicated that the primary detected element in all the pits examined was copper, with trace amounts of aluminum and silicon. It should be noted that all the mass was not recovered due to the fact that ICP-MS is not suitable for measuring elements such as oxygen and carbon.

Results of the ICP-MS analysis (**Table 3**) indicated that phosphate and sulfate concentrations were below the reporting level for our instrument in all samples. All metals concentrations looked normal with only one instance of elevated iron and manganese (Well 4-2). Lead concentrations were fairly low in all samples (except Well 5-4 where it was 6.0 ppb).

Copper pipe wall thickness measurements fell within the normal range for Type L copper (**Table 4**). The 10 readings for each pipe ranged between 94-105% of the specification and well within the listed tolerance. Hence the tube was not defectively thin.

Table 2: Summary of ICP-MS Data from Pit Analysis

Element	NY-1			
	Pit 1	*Pit 2*	*Pit 3*	*Pit 4*
Aluminum	0.06	0.06	0.04	0.02
Chloride	0.16	0.16	0.10	0.09
Copper	9.70	6.80	6.46	3.99
Silicon	0.15	0.14	0.11	0.06
Sulfur	0.55	0.33	0.36	0.25
Total	10.6	7.5	7.1	4.4
Original	14.4	9.9	9.7	5.9
% recovered	*73.7%*	*75.6%*	*72.8%*	*74.7%*
Element	**NY-2**	**NY-3**	**NY-4**	**NY-5**
Aluminum	0.04	0.06	0.09	0.15
Copper	4.97	1.89	6.38	7.84
Silicon	0.12	0.10	0.16	0.26
Total	5.2	2.1	6.7	8.3
Original	5.7	2.2	9.3	9.7
% recovered	*90.4%*	*94.4%*	*71.5%*	*85.4%*

Table 3: ICP-MS Data for 12 Well and 10 Plainview Water Samples

Sample ID	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Mn	Ni	Cu	Zn	Pb
	ppb	ppb	ppb	ppb	ppb	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Well 1-1	7,354	1,562	7.3	2,827	0.0	0.0	10.1	723	5,074	0.0	1.2	4.7	34.1	58.8	1.8
Well 1-2	7,357	1,439	4.6	2,791	0.0	0.3	9.3	706	11,210	0.9	0.3	4.3	4.8	37.1	0.3
Well 2-1	7,677	1,563	4.2	2,879	0.0	0.1	10.7	659	5,074	0.0	0.8	3.1	18.6	31.7	1.4
Well 3-2	10,440	2,416	1.1	3,167	0.0	0.2	14.3	671	7,100	75.8	9.8	2.7	10.9	41.2	0.1
Well 4-2	9,690	2,379	26.1	2,807	0.0	2.4	13.2	742	12,900	713.1	22.6	1.8	100.5	40.8	0.4
Well 4-3	8,683	2,040	1.2	2,995	0.0	0.0	10.8	670	6,031	2.1	0.6	2.2	8.0	40.4	0.5
Well 5-1	7,380	1,565	29.4	2,777	0.0	2.1	10.7	636	3,803	7.0	4.5	3.9	19.6	23.6	0.3
Well 5-2	9,880	2,432	37.5	2,899	0.0	2.9	13.9	816	6,112	32.0	8.6	5.0	26.9	50.7	2.2
Well 5-3	8,509	1,605	18.7	2,824	0.0	0.2	14.3	709	4,081	45.1	6.4	4.1	8.7	25.6	0.2
Well 5-4	10,380	1,839	33.2	2,986	0.0	0.5	16.3	710	4,559	5.4	6.8	4.9	23.6	81.7	6.0
Well 7-1	5,050	1,012	1.6	2,718	0.0	0.0	7.7	558	2,097	0.3	1.2	1.7	13.4	38.3	2.0
Well 7-2	4,859	886	4.2	2,730	0.0	0.7	9.1	552	1,868	7.5	2.7	1.7	21.4	55.3	1.5
Water District Office	8,261	1,566	93.7	2,897	0.0	1.7	12.5	663	6,273	59.8	4.3	3.6	5.6	9.0	0.3
Monte Pizza	8,455	1,715	28.1	2,838	0.0	1.4	12.9	681	5,051	17.2	6.1	4.3	7.4	12.1	0.3
Stunt Ford Road	8,323	1,766	22.4	3,032	0.0	0.0	11.1	673	9,953	10.4	1.0	1.7	2.3	4.1	0.5
Yogurt + Suert	8,965	2,005	11.9	3,121	0.0	0.0	12.1	677	10,250	23.7	1.1	5.3	10.4	21.1	0.0
Mama Lirro's	10,030	2,489	32.1	3,429	0.1	0.0	13.9	675	13,160	65.4	4.7	11.3	59.5	35.8	0.1
Optical Image	5,935	1,241	35.7	2,883	0.0	0.2	9.2	589	10,550	21.5	1.2	1.8	4.4	3.8	0.0
Kalda Lane	8,323	1,601	33.3	2,866	0.0	1.7	12.7	688	5,615	12.3	3.0	3.3	4.1	8.3	0.5
Dupont Street	7,780	1,590	34.4	2,992	0.0	0.2	11.1	676	13,250	16.4	1.0	2.3	6.5	6.3	0.4
STPA	7,369	1,744	53.4	2,971	0.0	0.1	10.4	732	17,940	32.3	2.2	3.4	7.3	8.8	0.1
Sunnyside Blvd	7,498	1,520	34.8	2,960	0.0	0.6	10.8	671	13,030	16.6	1.0	2.2	5.7	6.3	0.5

Table 4: Wall Thickness Measurement Summary

Pipe ID	Size (in)	Type	Spec. Thk (in)	Thk Tolerance (in)	Spec. Thk (mm)	Thk Tolerance (mm)	Avg Thk (mm)	std dev	% of spec
NY-1	0.75	L	0.045	0.004	1.143	0.102	1.124	0.043	98.3
NY-2	0.75	L	0.045	0.004	1.143	0.102	1.159	0.057	101.4
NY-3	0.75	??	0.045	0.004	1.143	0.102	1.200	0.025	105.0
NY-4	1.00	L	0.050	0.005	1.270	0.127	1.244	0.042	98.0
NY-5	1.00	L	0.050	0.005	1.270	0.127	1.198	0.069	94.3

CONCLUSIONS AND RECOMMENDATIONS

The results indicate a form of hot water pitting which is not yet clearly established in the scientific literature.

Even though the cause of pitting is unclear at this time, it is possible that a change in corrosion control might reduce the frequency of pitting. There are two possibilities that could be considered.

1) Increase in alkalinity
2) Addition of an orthophosphate corrosion inhibitor.

Higher alkalinity has been noted to decrease hot water pitting caused by sulfate in prior research.[2] No prior research has reported impacts of phosphate on hot water pitting. Moreover, there is potential concerns with microbial regrowth with phosphate, and there is additional cost for removing phosphate at wastewater treatment plants. While increased alkalinity may be more expensive, it is preferred as a possible solution, in an attempt to stop hot water pitting regardless of how it was started.

REFERENCES

1. Edwards, M., J. Rehring and T. Meyer. Inorganic Anions and Copper Pitting. ***Corrosion***, V. 50, No. 5, 366-372 (1994).

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

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

Figure A.1 – Pipe #1 interior surface (top) and exterior surface (bottom)

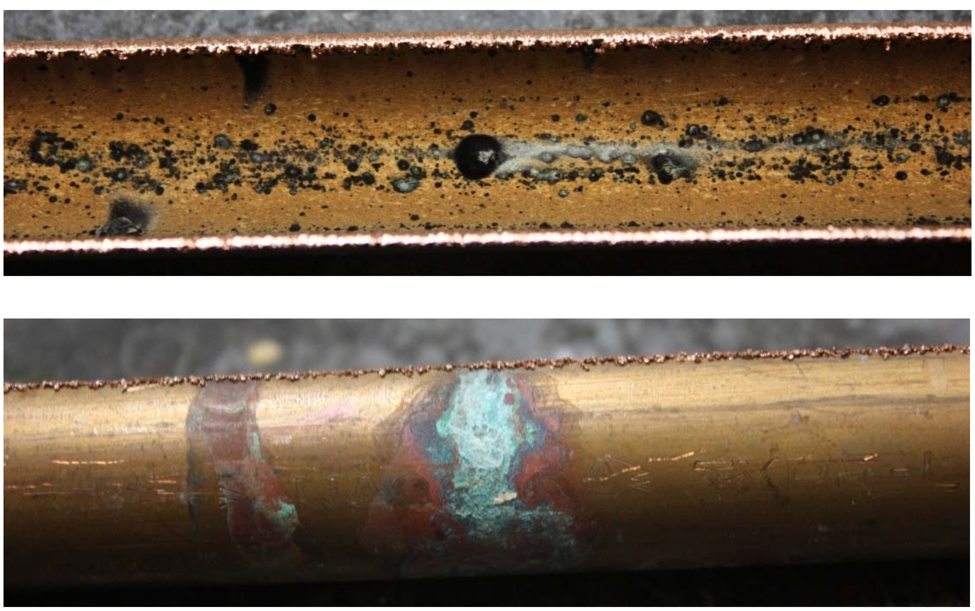

Figure A.2 – Pipe #2 interior surface (top) and exterior surface (bottom)

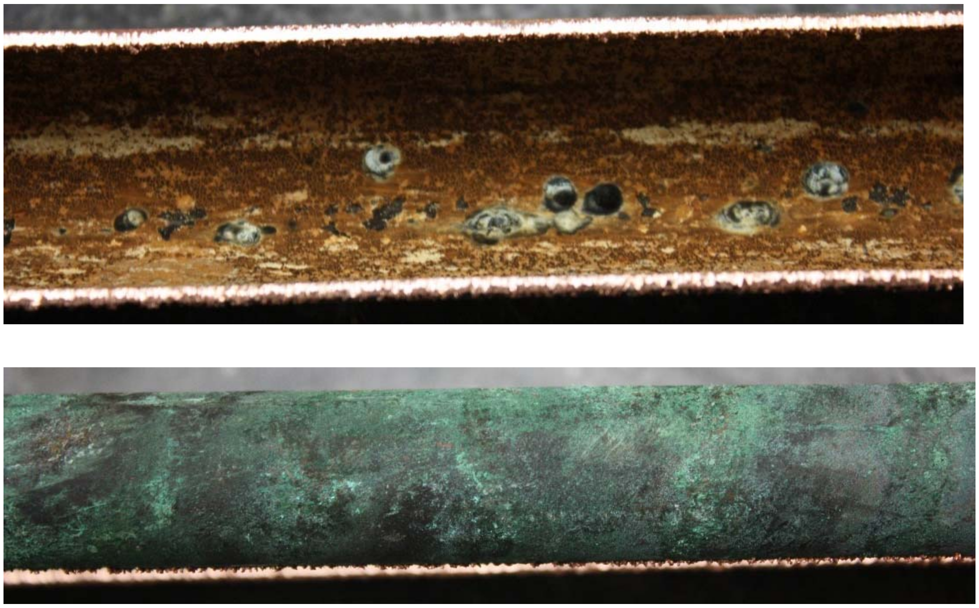

Figure A.3 – Pipe #3 interior surface (top) and exterior surface (bottom)

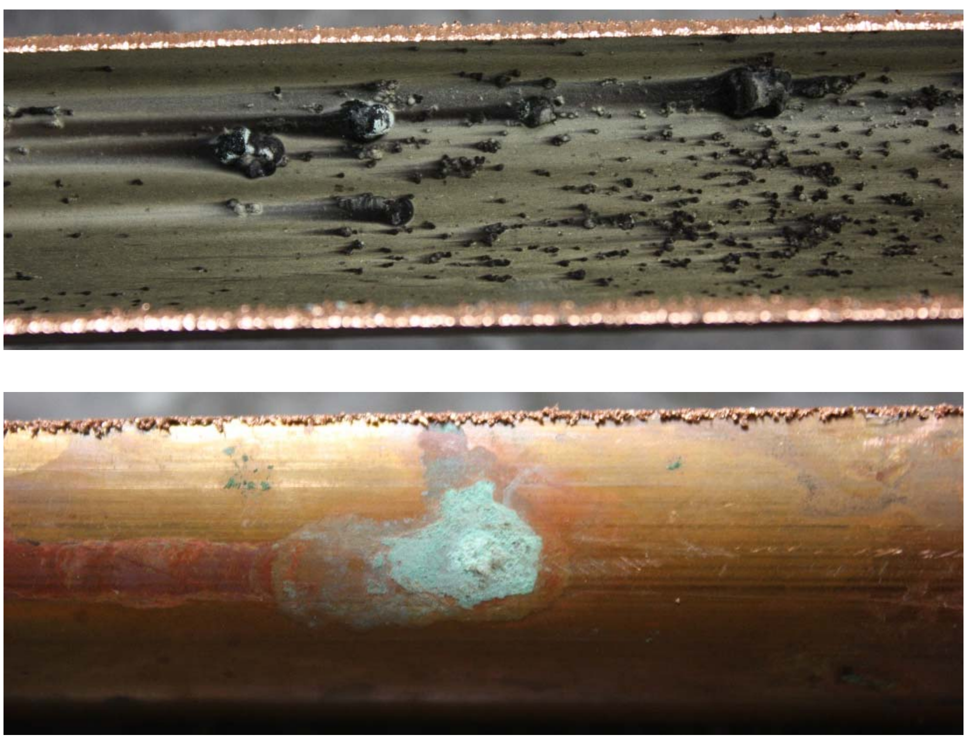

Figure A.4 – Pipe #4 interior surface (top) and exterior surface (bottom)

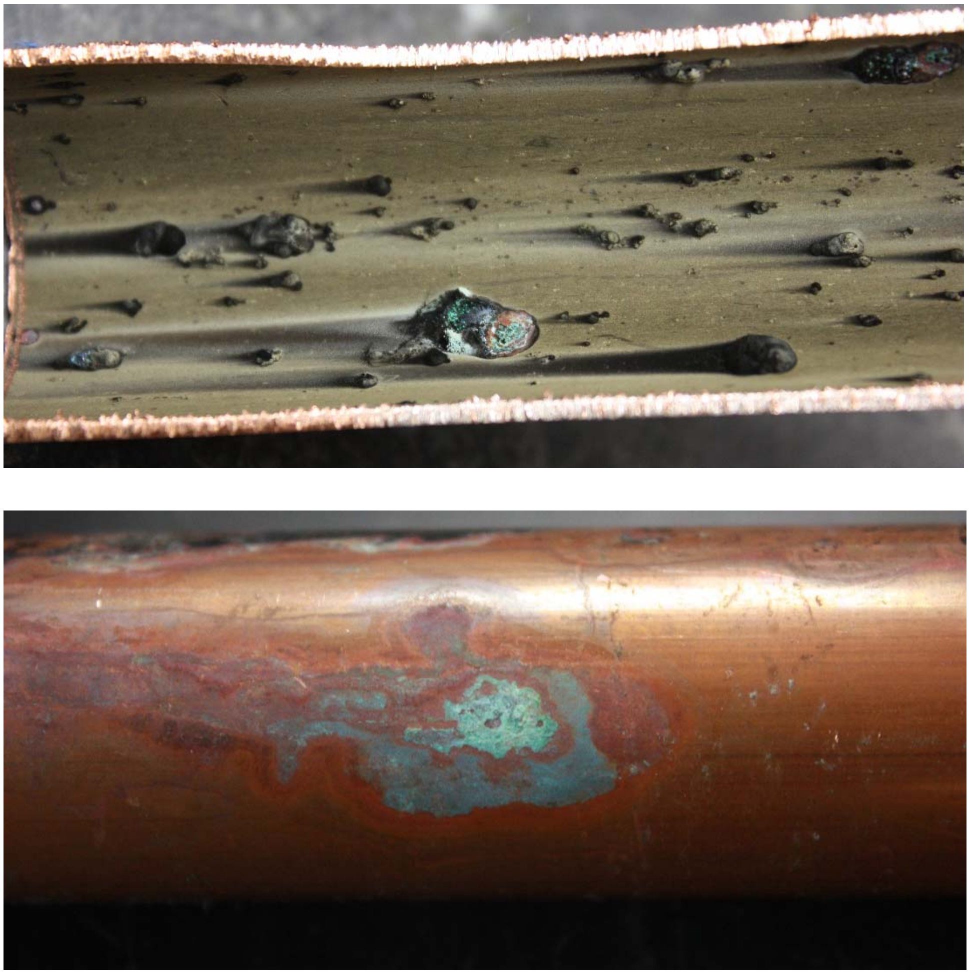

Figure A.5 – Pipe #5 interior surface (top) and exterior surface (bottom)