

M. E. Williams and Associates, Inc.

"Excellence in Metallurgical Engineering"

12825 385th Avenue
Waseca, MN 56093

November 16, 2016

USA Coil & Air, Inc.
Warranty/Claims Manager
P.O. Box 578
Devault, PA 1932

Report Number: 16-4686

Dear Sirs:

Subject

Failure analysis of two steam coil sections used in a steam heating system, and analysis of two water samples removed from the system containing the failed coils. The water samples were examined by visual examination, scanning electron microscopic examination, energy dispersive x-ray analysis, and anion analysis. The copper tubing in the failed coil samples was examined by visual examination, scanning electron microscopic examination, energy dispersive x-ray analysis, and metallographic examination.

Feed Water Analysis

Visual Examination

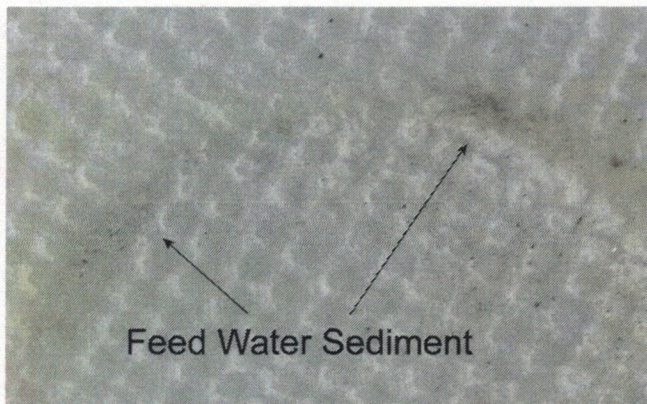


Figure 1 – Feed Water Sediment from Front by Dock Water Sample

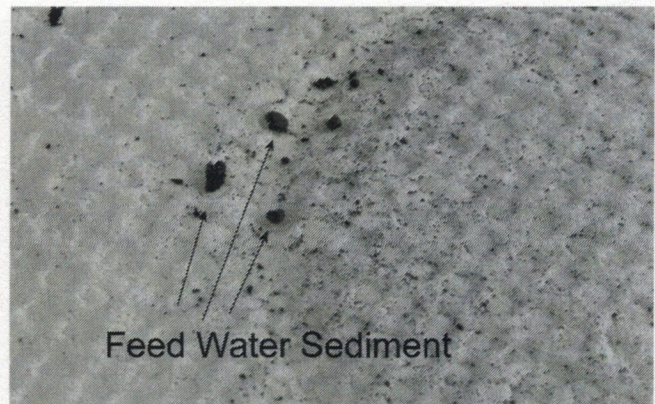


Figure 2 – Feed Water Sediment from CIP Water Sample

There was a small amount of sediment in the feed water sample labeled Front by Dock. Some of the sediment is shown in Figure 1.

There was considerably more sediment in the CIP Water Sample. Some of that sediment is shown in Figure 2. Figure 3 shows some of the sediment sticking to a magnet, indicating that the black material in

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the sediment was magnetite, magnetic iron oxide (Fe₃O₄). Some of the magnetic iron oxide is in the form of spheres.

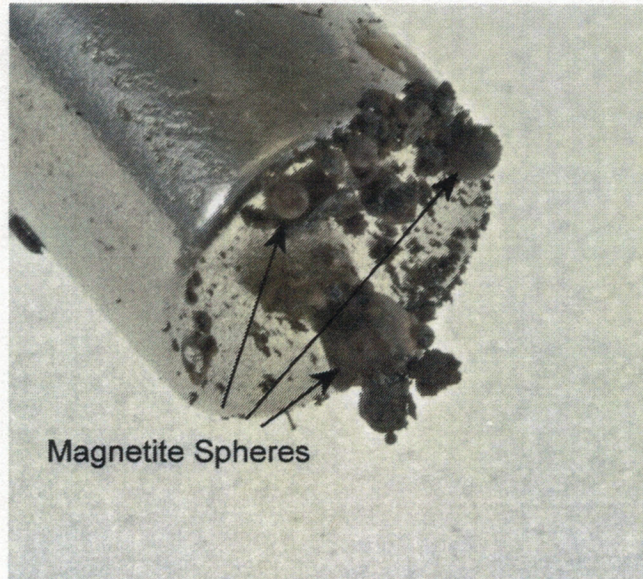


Figure 3 – Sediment from CIP Water Sample

Anion Analysis of Feed Water Samples

The feed water samples were analyzed by EPA Method 9040C, for anions associated with the corrosion of copper. The results of the analysis are given in the table that follows.

Anion Analysis of Feed Water (mg/L or ppm)			
Ion/Sample	Dock	CIP	Detection Limit
Bromide	<0.20	<0.20	0.20
Chloride	0.13	0.14	0.10
Fluoride	<0.020	0.036	0.020
Nitrate as NO ₃	<0.10	<0.10	0.10
Nitrate as N	<0.023	<0.023	0.023
Nitrite as NO ₂	<0.20	<0.20	0.20
Nitrite as N	<0.061	<0.061	0.061
Phosphate as PO ₄	<0.20	<0.20	0.20
Sulfate as SO ₄	<0.10	<0.10	0.10

The chloride levels are low enough that they should not be corrosive to copper or 304L stainless steel. Fluoride level is not a concern because most fluorides are insoluble. The presence of chlorides and fluorides indicates that the feed water is made up from RO water. Low concentrations of chlorides often

make it through RO units. The pH of the water sample Front by Dock was 9.5, and the pH of water sample CIP was 9.4.

There were no corrosive anions found in the feed water samples provided.

Scanning Electron Microscopic and EDS Analysis

The sediment material from the two water samples was examined by scanning electron microscope with an energy dispersive x-ray analysis unit to determine the composition and physical nature of the sediment.

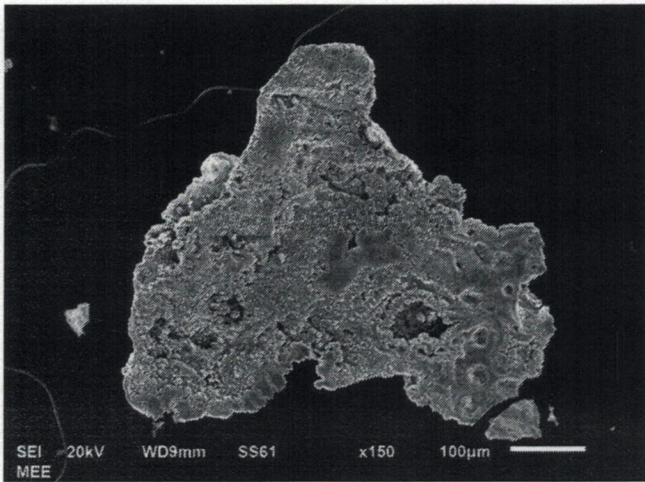


Figure 4 – 150X Feed Water Sediment, Front of Dock Sample

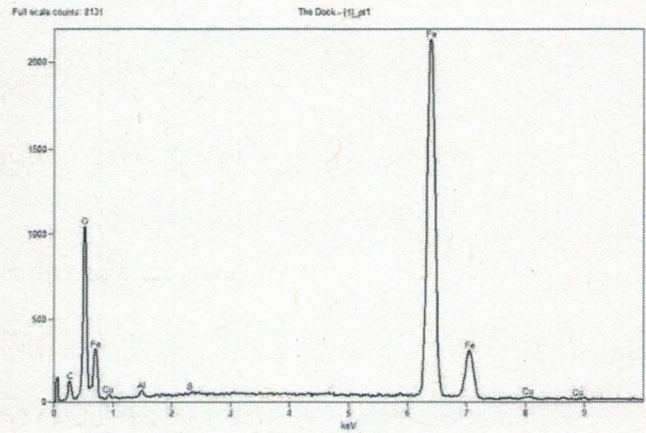


Figure 5 – Spectrum of Sediment shown in Figure 4 – Front of Dock Sample

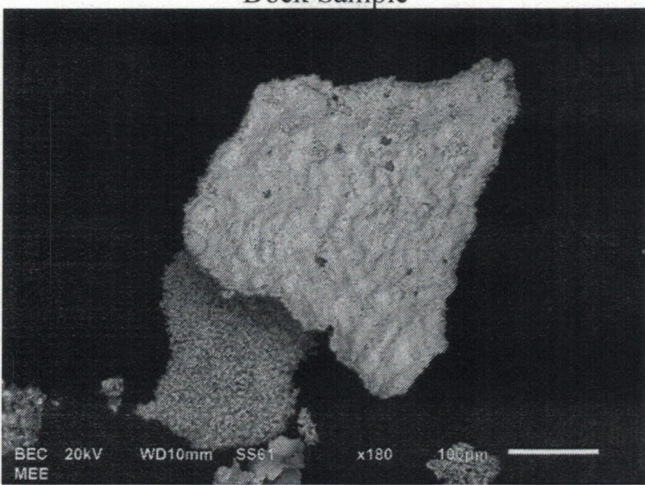


Figure 6 – 180X Feed Water Sediment, Front of Dock Sample

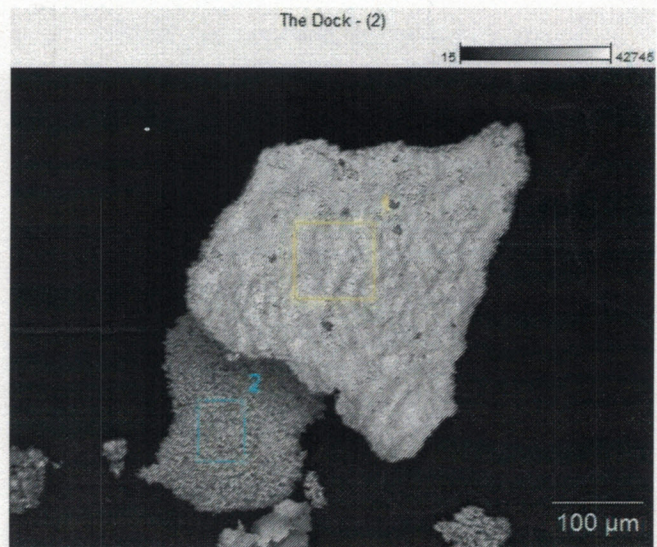


Figure 7 – 180X Analysis Locations, Front of Dock Sample

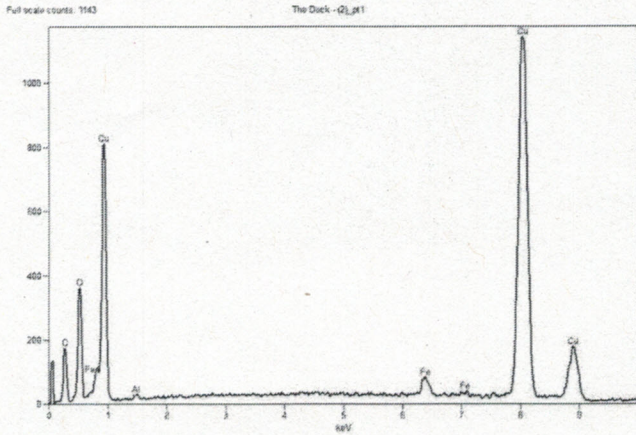


Figure 8 – Spectrum of Figure 7, Location 1

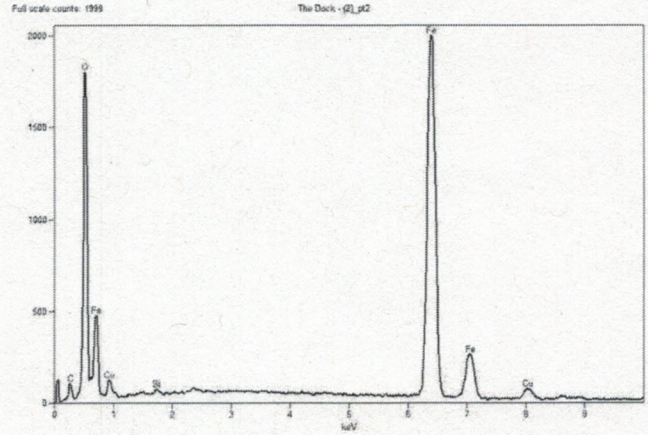


Figure 9 – Spectrum of Figure 7, Location 2

Front of Dock Sediment Analysis (Percent by Weight)			
Element/Location	Figure 4	Figure 7 - 1	Figure 7 - 2
Carbon	2.7	3.7	0.7
Oxygen	13.6	7.7	21.4
Aluminum	0.4	0.2	N/A
Silicon	N/A	N/A	0.3
Sulfur	Trace	N/A	N/A
Iron	82.2	1.6	73.2
Copper	1.1	86.8	4.4
Spectrum	Figure 5	Figure 8	Figure 9

The presence of aluminum is a potential problem with the feed water.

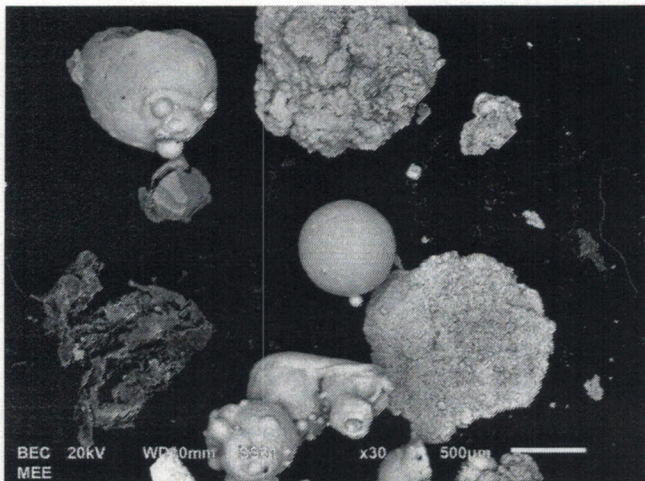


Figure 10 – 30X Feed Water Sediment CIP, Area 1

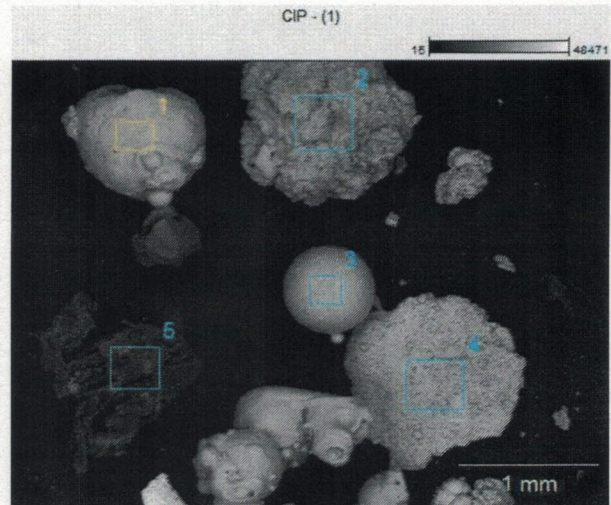


Figure 11 – 30X Analysis Locations, CIP Water Sediment, Area 1

The sediment from the CIP location was somewhat different than that from the Dock location. Figure 10 shows the variety of structures that were found. Figure 11 shows the locations of the analysis. The spectra are shown in Figures 12 through 16, and the semi-quantitative analysis is given in the table that follows.

CIP Sediment Analysis Area 1 (Percent by Weight)					
Element/Location	1	2	3	4	5
Carbon	2.4	1.4	1.3	1.6	53.7
Oxygen	31.5	23.3	26.4	18.8	23.5
Aluminum	0.7	0.3	0.3	0.4	0.4
Silicon	0.5				
Phosphorous	0.2				
Sulfur	0.1				
Titanium	0.2				
Manganese	0.8		1.1		
Iron	63.7	74.0	70.3	2.6	20.4
Copper		1.0	0.5	76.6	2.0
Spectrum	Figure 12	Figure 13	Figure 14	Figure 15	Figure 16

Location 1 appears to be a piece of carbon steel. Aluminum and titanium are often used as grain refiners in steel. Locations 2 and 3 are iron oxide nodules. Location 4 is a piece of copper oxide scale. Location 5 is an iron rich organic material. Each of these particles were formed as a result of corrosion in the system. A likely source of the aluminum is the steel piping and tubing in the system.

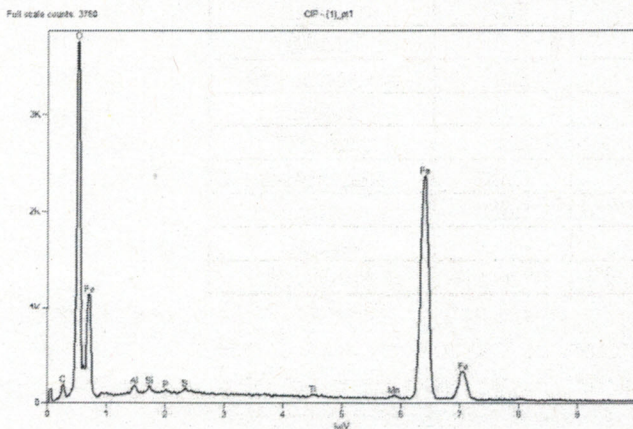


Figure 12 – Spectrum of CIP Area 1, Location 1

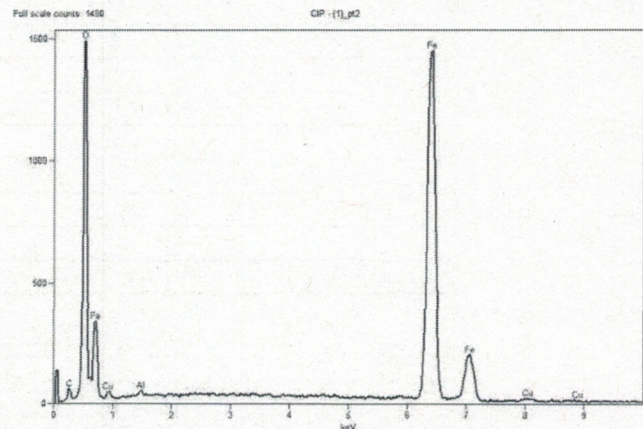


Figure 13 – Spectrum of CIP Area 1, Location 2

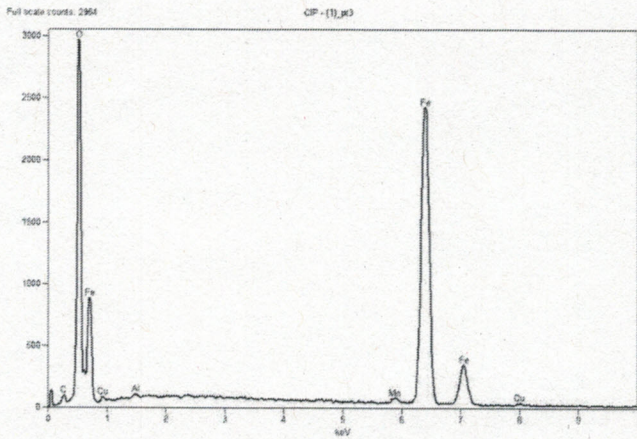


Figure 14 – Spectrum of CIP Area 1, Location 3

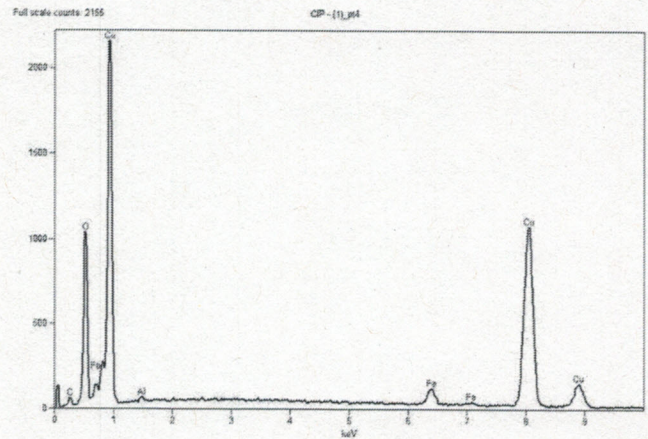


Figure 15 – Spectrum of CIP Area 1, Location 4

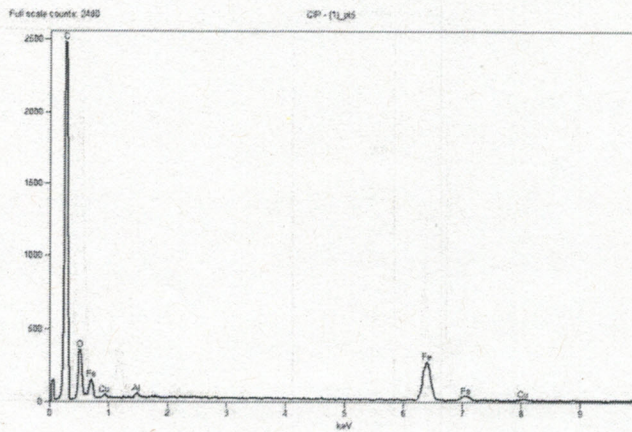


Figure 16 – Spectrum of CIP Area 1, Location 5

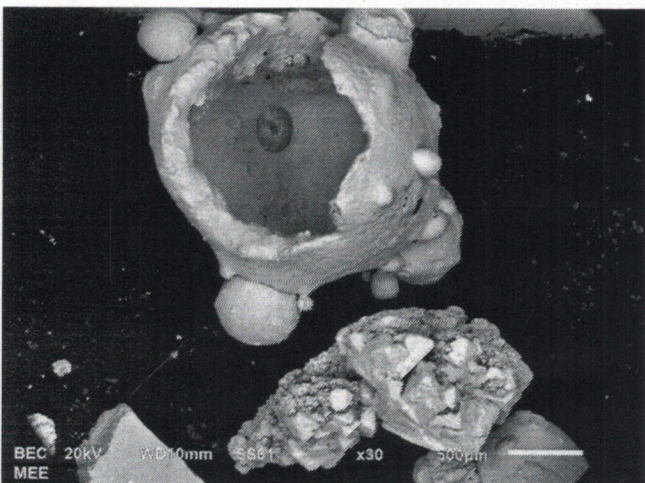


Figure 17 – 30X Feed Water Sediment CIP, Area 2

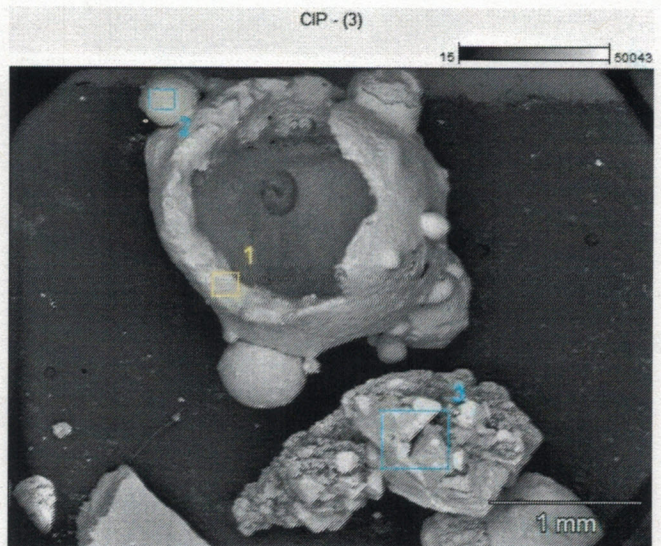


Figure 18 – 30X Feed Water Sediment CIP, Area 2, Analysis Locations

The hollow nodule shown in Figure 17 indicates there may be bacteria in the feed water. The pH of the feed water may be high enough to prevent bacteria growth, but localized pH may allow bacterial growth. Location 3, Figure 18, had to be reanalyzed to obtain a good spectrum, because the x-rays were blocked by the hollow nodule. The reanalysis is reported as Location 4 in the table and spectra that follow. The semi-quantitative analysis is given in the table that follows.

CIP Sediment Analysis Area 2 (Percent by Weight)			
Element/Location	1	2	4
Carbon	1.6	0.9	2.4
Oxygen	27.1	29.0	19.9
Aluminum	0.3	0.7	0.6
Silicon	0.6		
Phosphorous	0.5		
Sulfur	0.2		
Manganese	0.5		
Iron	69.2	68.9	1.9
Copper		0.5	75.2
Spectrum	Figure 19	Figure 20	Figure 21

The hollow nodule, Location 1, appears to be oxidized steel. Location 2 is iron oxide, and Location 4 is a group of copper oxide crystals. Aluminum was present in all three locations.

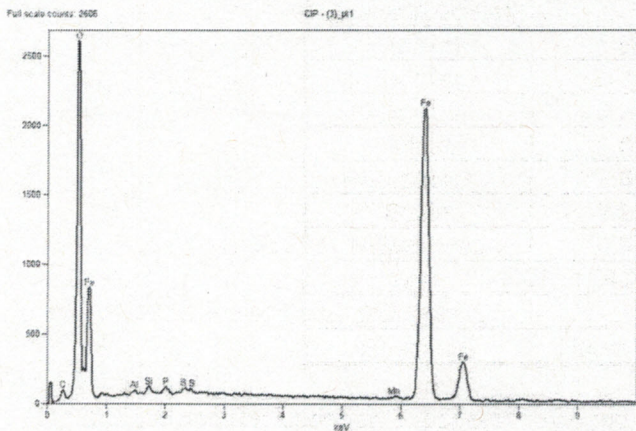


Figure 19 – Spectrum of CIP Area 2, Location 1

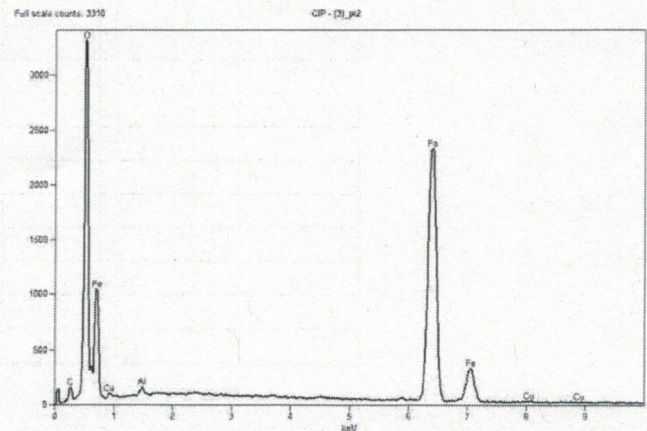


Figure 20 – Spectrum of CIP Area 2, Location 2

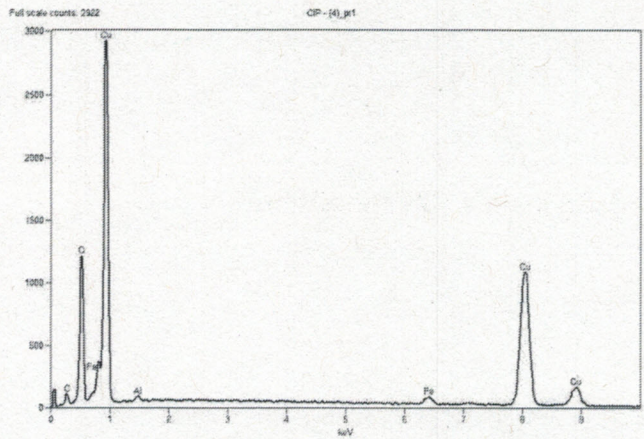


Figure 21 – Spectrum of CIP Area 2, Location 4

Failure Analysis of Copper Tubing

Visual Examination

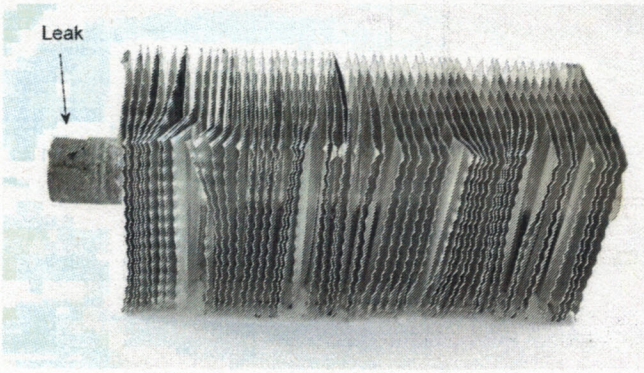


Figure 22 – Coil Sample 1



Figure 23 – Leak, Coil Sample 1



Figure 24 – Tube Sections, Sample 1

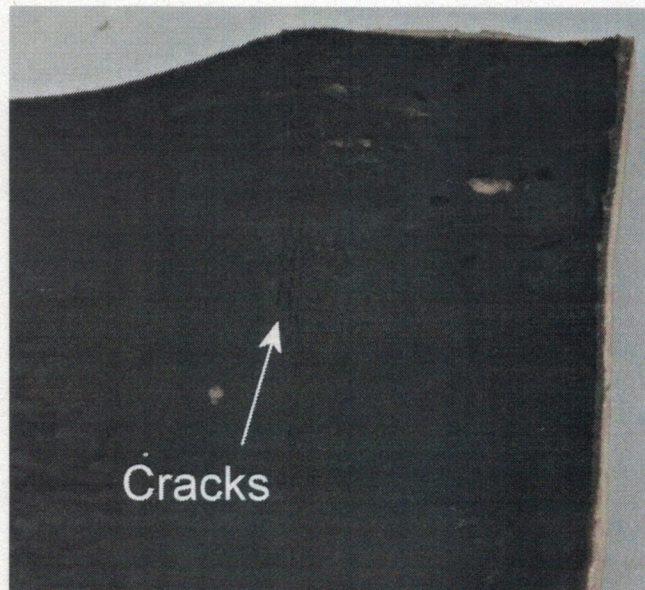


Figure 25 – Crack in I.D. Tube Sample 1

Figure 22 shows Coil Sample 1. The leak was on the top side of the tube, and the tube was located on the top of the coil. It was the last tube that the steam would pass through in the coil. There was considerable thinning of the copper tubing associated with the leak, Figures 23 and 24. Thinning of the tubing is usually the result of fine water droplets in the steam that impinge on the surface and cause erosion. Figure 25 shows cracks on the inside diameter of the tube. This sample was from the tube on the right in Figure 24. Cracking was likely the result of embrittlement of the copper tube and had nothing to do with erosion.

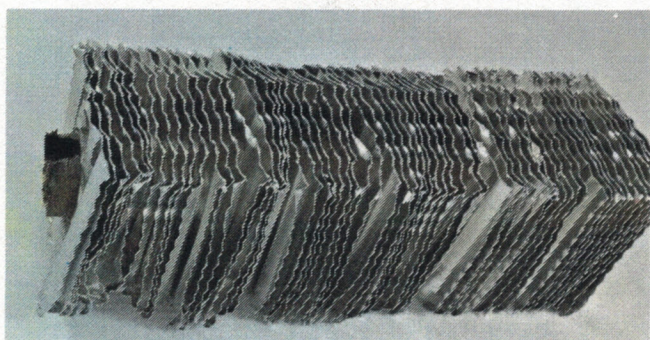


Figure 26 – Coil Sample 2

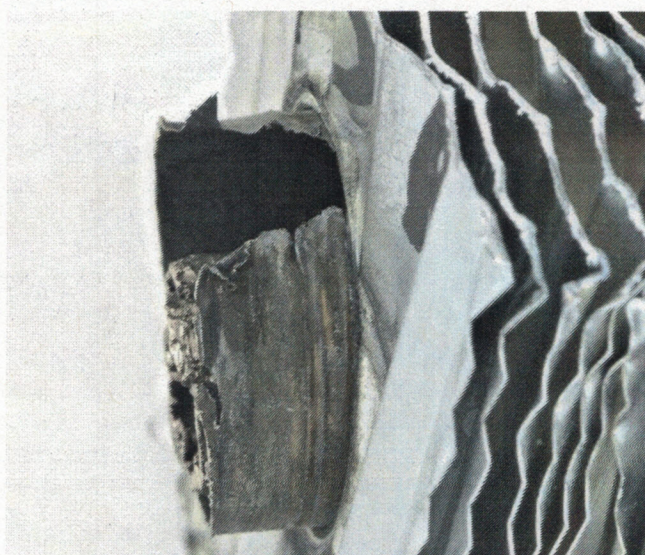


Figure 27 – Leak in Coil Sample 2

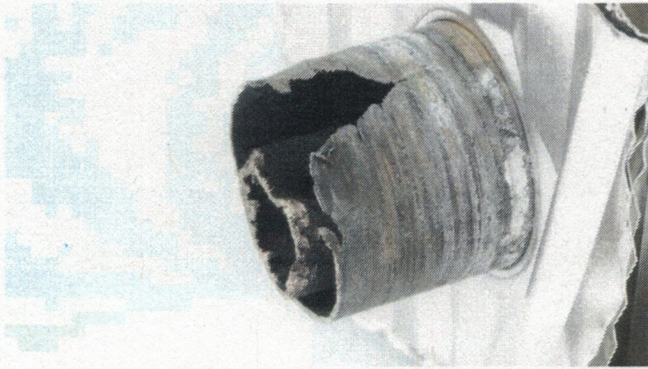


Figure 28 – Leak in Coil Sample 2



Figure 29 – Inside Diameter of Coil Sample 2

Coil Sample 2, Figure 26, was also taken from the top row of the coil. The leak on the top side of the tubing appeared to be the result of thinning. Figures 27 and 28 show the leak, which was on the top side of the tube. The apparent cause of leakage was erosion due to condensate in the steam. The tube did not crack when it was opened for examination, Figure 29. What appears to be cracks was the result of the oxide scale flaking off.

Scanning Electron Microscopic and EDS Analysis

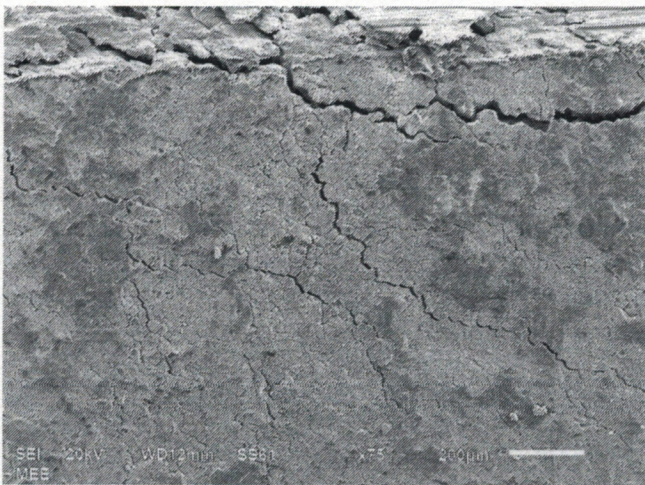


Figure 30 – 75X Intergranular Cracking I.D. Coil Sample 1

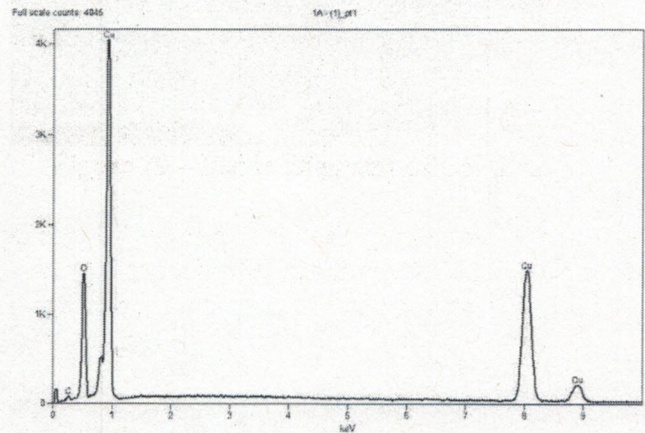


Figure 31 – Spectrum of Surface Shown in Figure 30
Coil Sample 1

The cracking on the inside diameter of Coil Sample 1 is shown in Figure 30. The cracking mode is intergranular, which is a brittle fracture mode. The most common cause of intergranular cracking in copper

tubing is ammonia. Figure 31 is the spectrum of the surface shown in Figure 30. Only three elements are present: carbon, oxygen, and copper. Ammonia and other nitrogen compounds are very hard to detect by energy dispersive x-ray analysis, but the intergranular cracking is a key indicator that they were present.

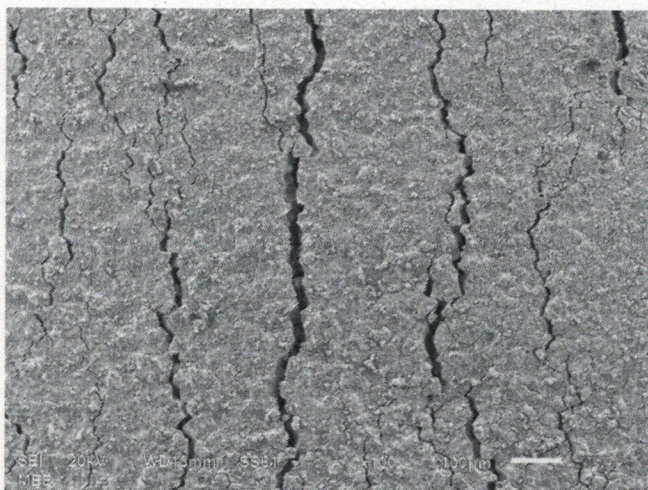


Figure 32 – 37X Intergranular Cracking on I.D. of Coil Sample 1

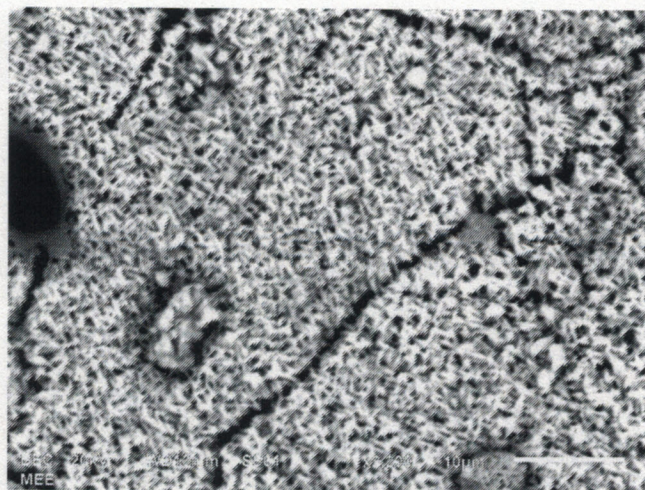


Figure 33 – 2200X I.D. Surface of Coil Sample 1

The intergranular cracking on the inside diameter of Coil Sample 1 is clearly shown in Figure 32. Figure 33 shows the nature of the oxide formation on the inside diameter of Coil Sample 1. Figure 34 is the energy dispersive x-ray spectrum of the surface area shown in Figure 32. This was the only location where aluminum was detected on the inside diameter of the copper tubing. The other elements were carbon, oxygen, and copper.

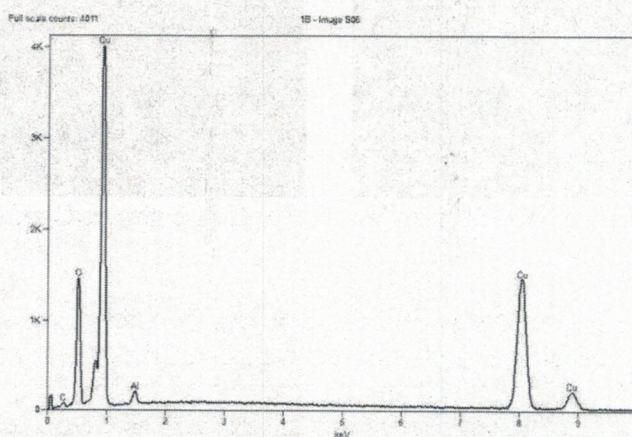


Figure 34 – Spectrum of the Surface Shown in Figure 32

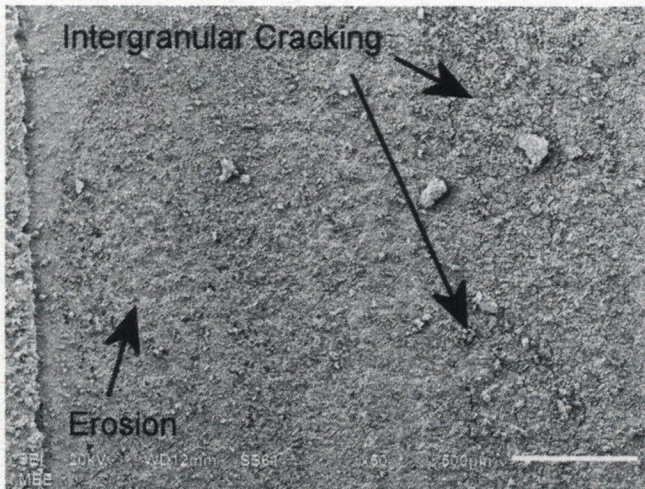


Figure 35 – 50X I.D. of Coil Sample 2

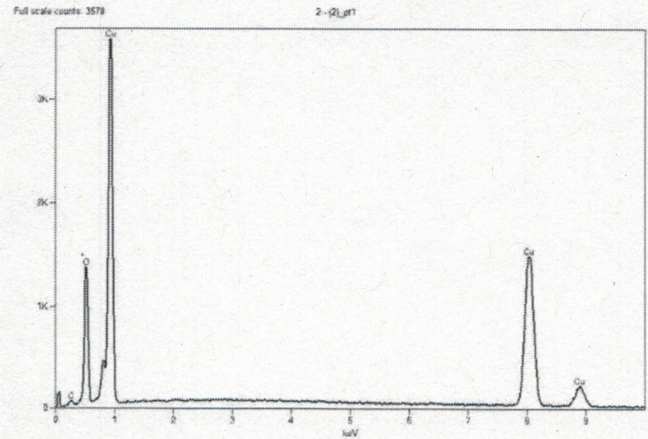


Figure 36 – Spectrum of Surface shown in Figure 35

Figure 35 shows a location on the inside diameter of Coil Sample 2. The thick oxide scale had flaked off the copper at this location. There was evidence of erosion and evidence of intergranular cracking present. Figure 36 shows the spectrum of the area shown in Figure 35. The elements present were carbon, oxygen, and copper.

Note that the likely source of the carbon is carbon dioxide in the air. It is typically detected on metal and metal oxide surfaces by energy dispersive x-ray analysis.

Metallographic Examination

The magnification shown for the photos is the magnification at which the photos were taken. The photos shown in this report may be smaller or larger in size than the originals.

Figures 37 and 38 show intergranular stress corrosion cracking in the copper from Coil Sample 1. The intergranular stress corrosion cracking occurred in most locations on the inside diameter of the tube. There was thinning at the top of the tube. The bottom of the tube did not show thinning. Intergranular stress corrosion cracking destroys the metallic bonds at the grain boundaries, as shown in the photos. Any force to the grains will likely cause them to break free from the tube surface. The combination of erosion and intergranular stress corrosion cracking would result in rapid thinning of the copper tubing.

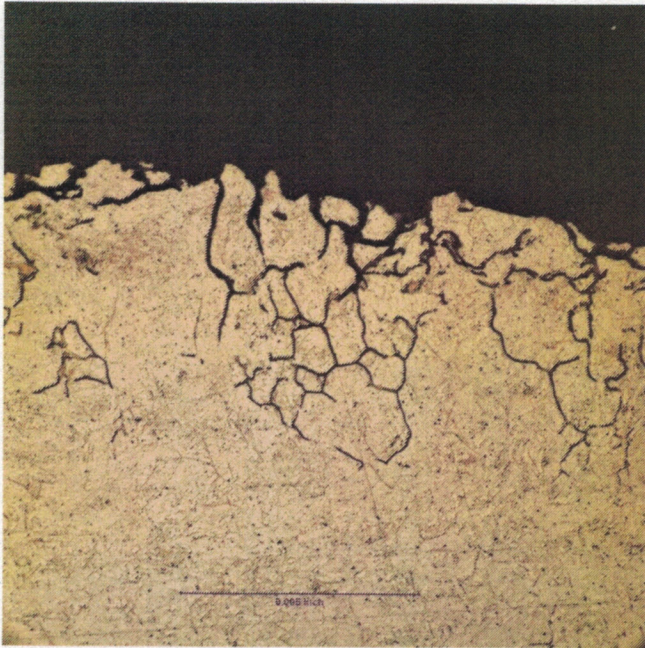


Figure 37 – 400X Intergranular Stress Corrosion Cracking of Top Side of Copper Tube from Coil Sample 1

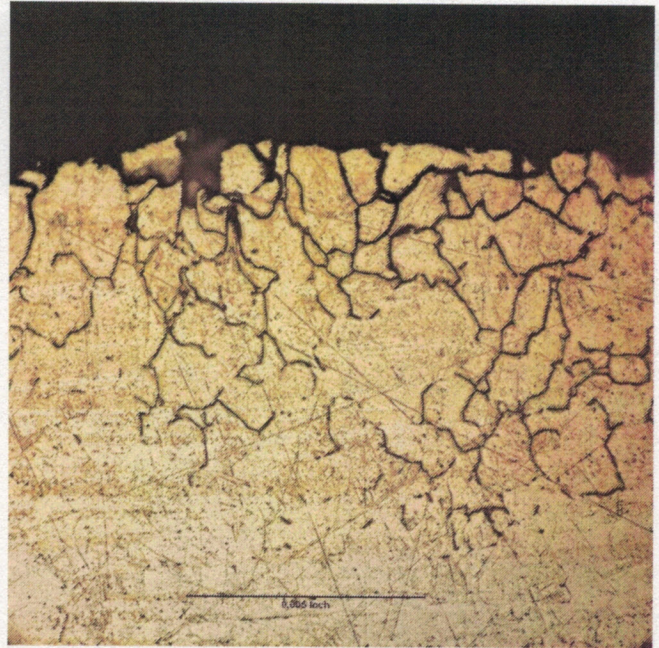


Figure 38 – 400X Intergranular Stress Corrosion Cracking of Bottom Side of Copper Tube from Coil Sample 1

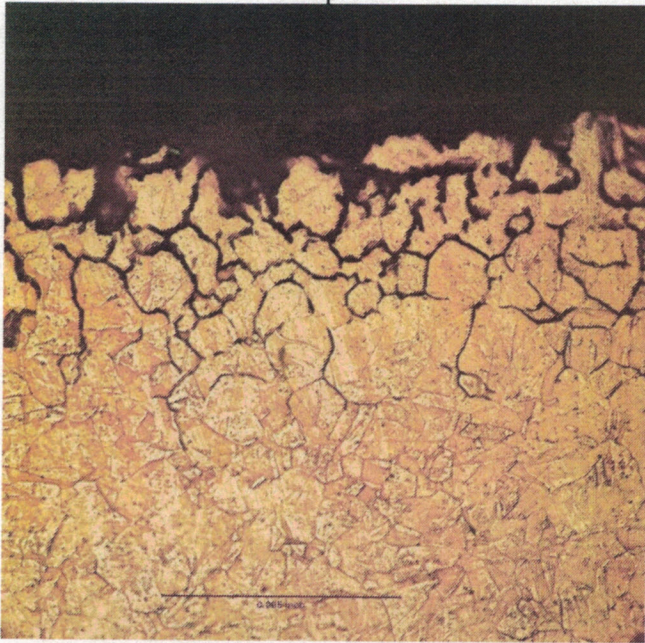


Figure 39 – 400X Intergranular Stress Corrosion Cracking of Top Side of Copper Tube from Coil Sample 2

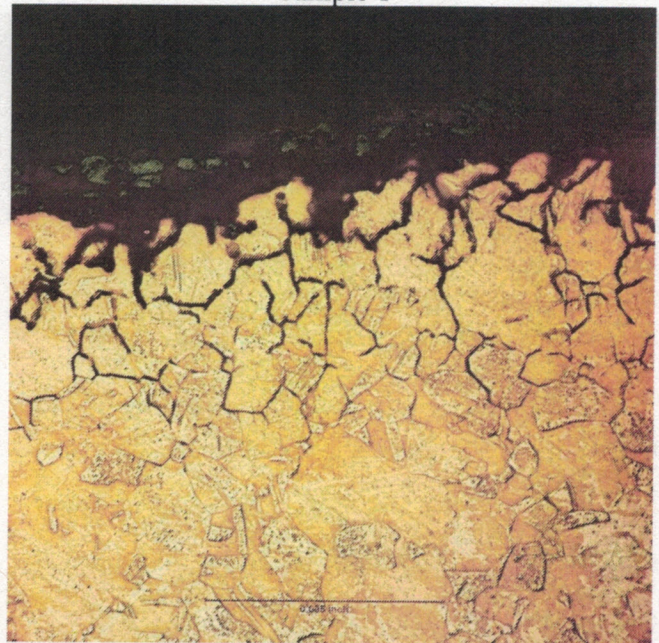


Figure 40 – 400X Intergranular Stress Corrosion Cracking of Bottom Side of Copper Tube from Coil Sample 2

The copper tube from Coil Sample 2 showed the same conditions found in the sample from Coil Sample 1. The most common cause of intergranular stress corrosion cracking in copper is ammonia. Even at room temperature, moist ammonia will cause stress corrosion cracking in copper tubing.

Discussion

The water analysis did not show any indication of nitrates or nitrites which can also cause stress corrosion cracking in copper. The energy dispersive x-ray analysis did not find any trace of nitrogen compounds. The only evidence that corrosive nitrogen compounds were present is the intergranular stress corrosion cracking. The intergranular cracking was shown by the scanning electron microscopic and metallographic examinations of the copper tubing. Because no nitrogen compounds were detected, ammonia is the most likely cause of the cracking.

Hydrazine, N_2H_4 , is used to deoxidize boiler feed water. Hydrazine in the boiler feed water promotes the formation of iron oxide in the form of magnetite, Fe_3O_4 , instead of hematite, Fe_2O_3 . Hematite is the normal iron oxide that forms during rusting of iron in water and is not magnetic. The sediment from the two water samples was magnetic, indicating that hydrazine or a similar compound was used in deoxidizing the boiler feed. Hydrazine can decompose into ammonia and nitrogen gas. Decomposition can happen at a temperature of 572° F. or greater. Thin films of copper and fine copper flakes can act as a catalyst for the decomposition of hydrazine to ammonia and nitrogen gas. Copper oxides were found in the boiler feed sediment, indicating that fine copper particles could also have been present.

If there are bacteria in the feed water, the bacteria can produce ammonia when they decompose.

I would recommend checking the thickness of the steel tubing in the heating system to ensure that thinning of the tubing has not occurred. The thickness can be checked by using ultrasonic testing, if the tubing and piping are accessible. There could be erosion of the steel tubing as the result of the age of the system. Do Not Remove asbestos insulation, if present.

There does not appear to be any corrosive elements present that would cause corrosion of 304L stainless steel. Chlorides are the main cause of corrosion of 304L stainless steel and there does not appear to have been any chlorides in the heat exchangers. Replacing the heat exchangers with ones made from 304L stainless steel will mean that the entire heating system will not have to be cleaned.

Conclusions

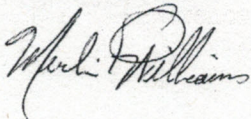
1. The copper tubing failed by a combination of erosion and stress corrosion cracking.
2. The boiler feed water contained only a very small amount of chlorides, ~0.13 ppm, which would have no effect on copper tubing.
3. The presence of magnetite indicates that hydrazine or a similar compound was used to deoxidize the boiler feed water. Hydrazine can decompose into ammonia and nitrogen gas.

Recommendations

1. Replace the heat exchangers with heat exchangers fabricated from 304L stainless steel.
2. Check the steel tubing in the system by ultrasonic testing to determine the thickness of the steel tubing and piping, if they are accessible.

If you have any questions regarding this report, please contact me.

Sincerely yours,



Merlin E. Williams, P.E.
President