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Case Study: Stainless Steel Ammonia Evaporator Coil

By

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Scope of Examination

Examination of a Stainless Steel Ammonia Evaporator Coil to determine the cause of leaking. The coil was examined by visual examination, scanning electron microscopic examination, energy dispersive x-ray analysis (EDX), GCMS analysis, and metallographic examination.

Note: Recent increases in the price of nickel may present future problems with austenitic stainless steels. High cost of nickel has resulted in problems in the past.

Visual Examination

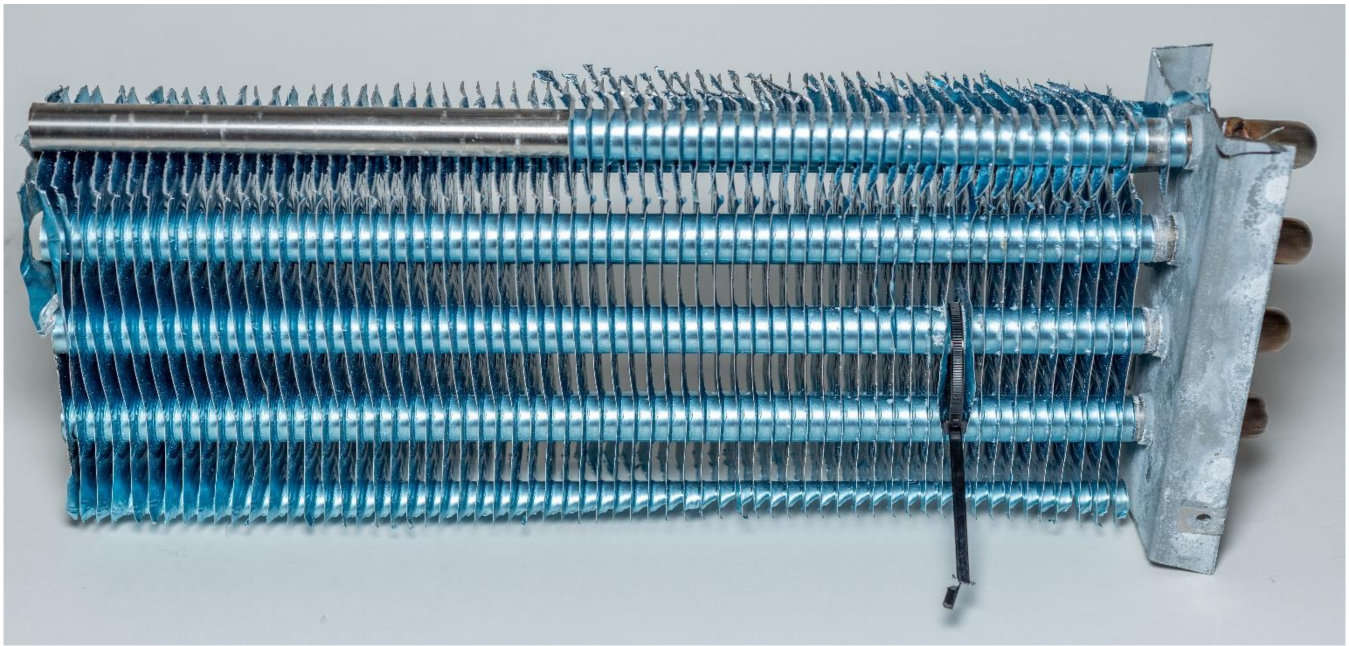

Figure 1 – Coil Sample As-Received

Figure 1 shows the section of the evaporator coil as-received. The leak location was marked with a black cable tie.

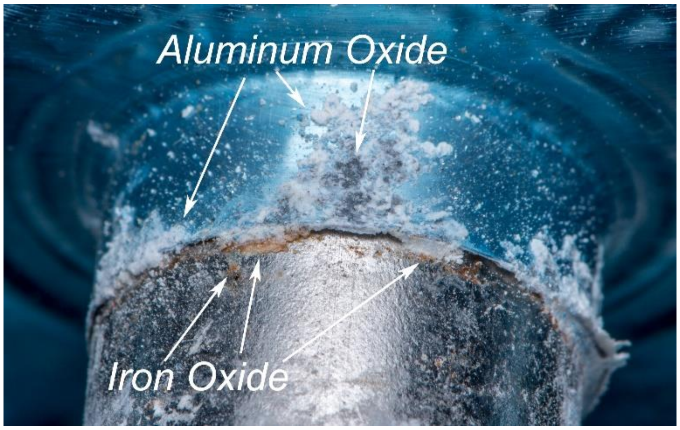

Figure 2 – Leak Location and Blue Fin Material

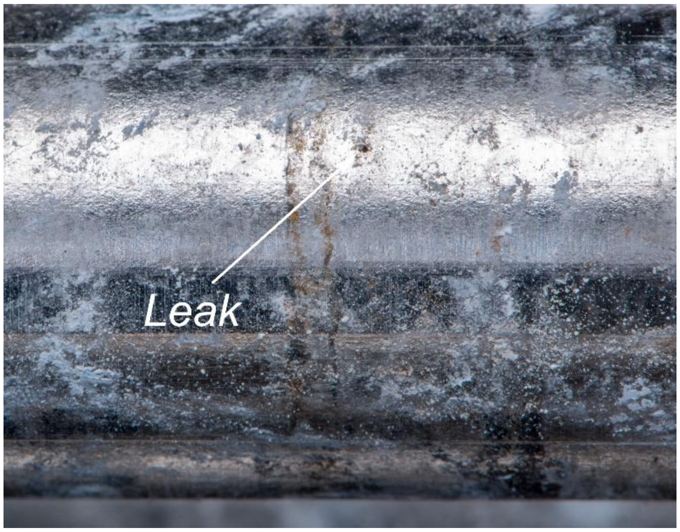

Figure 3 – Leak Location

The red-brown material found, Figure 2, was primarily iron oxide, the source of which was unknown. Figure 3 shows the leak area after the fin was removed.

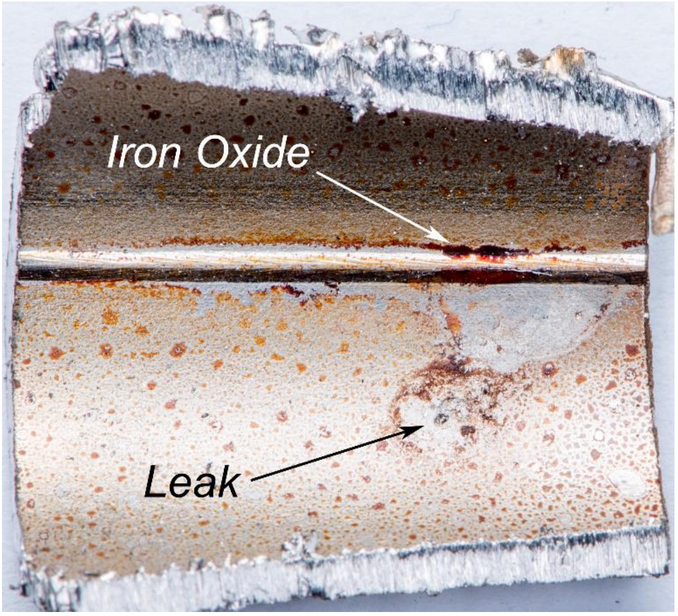

Figure 4 – Leak Location I.D.

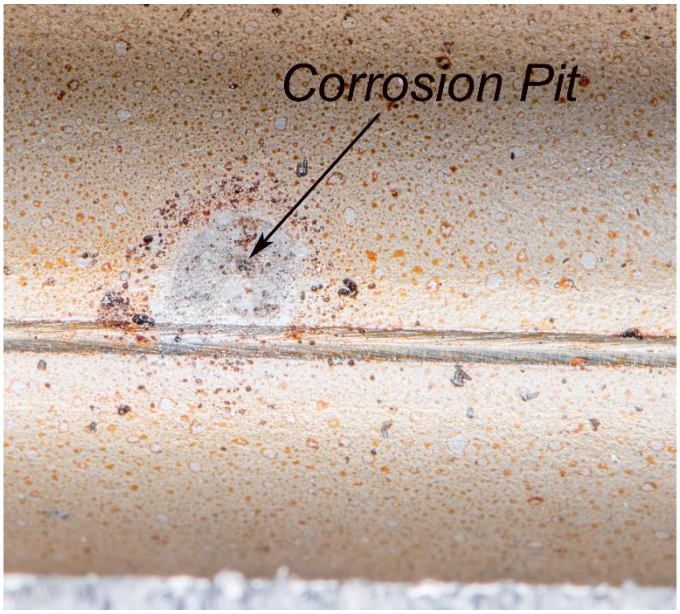

Figure 5 – Corrosion Pit on Sample 1 I.D.

The inside of the tube with the leak location indicated is shown in Figure 4. The red/brown material was mostly iron oxide. Figure 5 shows a location in the same tube where there was pitting corrosion, but no leak. The longitudinal ridge running the length of the tubing indicates that this was welded tubing.

Scanning Electron Microscopic Examination

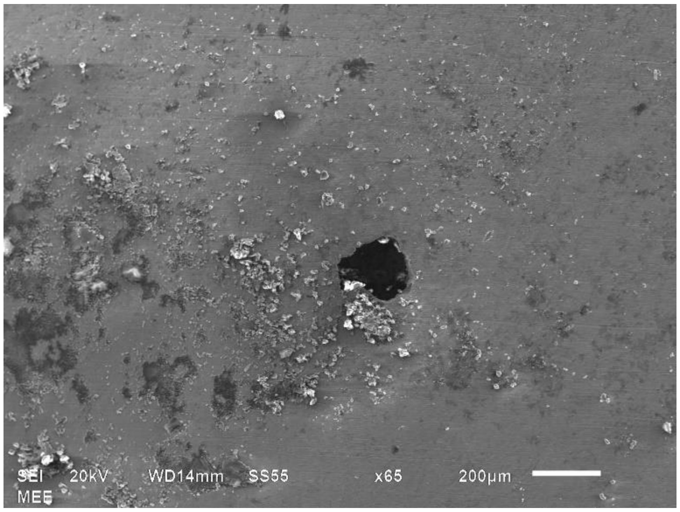

Figure 6 – 65X Leak O.D.

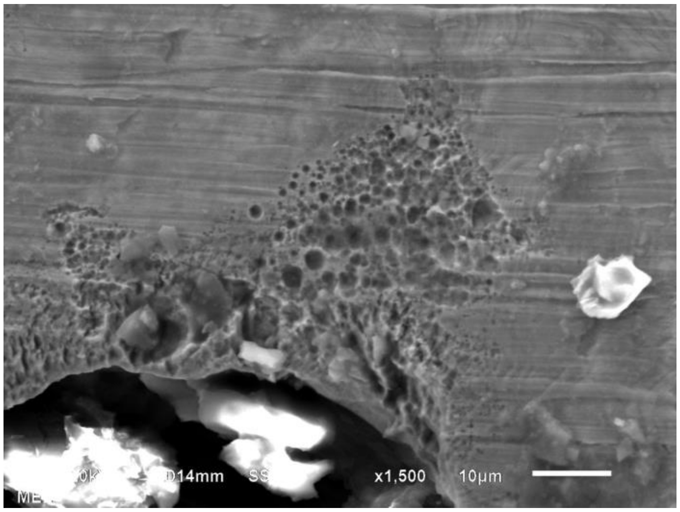

Figure 7 – 1500X Pitting Corrosion on Leak Periphery on Sample 1 O.D.

Figure 6 shows the leak on the outside diameter of the tube. Figure 7 shows pitting corrosion next to the hole. Pitting corrosion in 304 stainless steel is usually caused by wet chlorides.

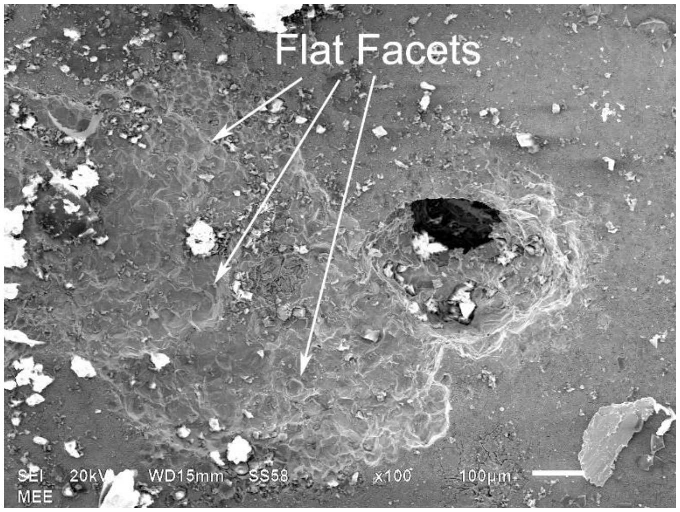

Figure 8 – 100X Corrosion and Leak Location Tube I.D.

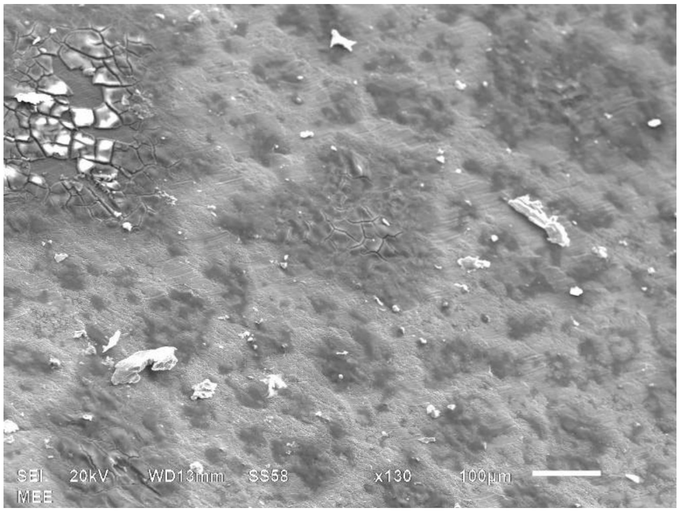

Figure 9 – 130X Deposits I.D.

Figure 8 shows the leak on the inside diameter of the tube. The flat facets in the area indicated that the corrosion was intergranular pitting corrosion. In order for intergranular pitting corrosion to occur, the stainless steel needs to be sensitized. Sensitization of austenitic stainless steels is caused by the formation of grain boundary chromium carbides when the material is heated during welding, or some other high temperature process, and the carbon content is 0.04% or greater.

Figure 9 shows deposits on the inside diameter of the tube.

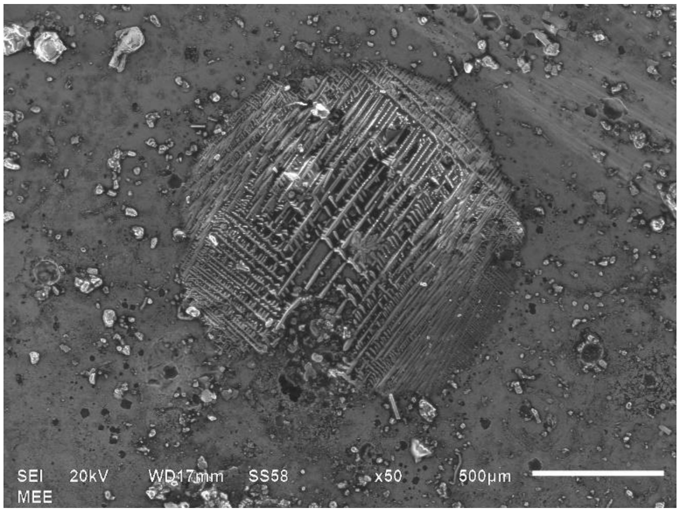

Figure 10 – 50X Crystaline Growth Tube I.D.

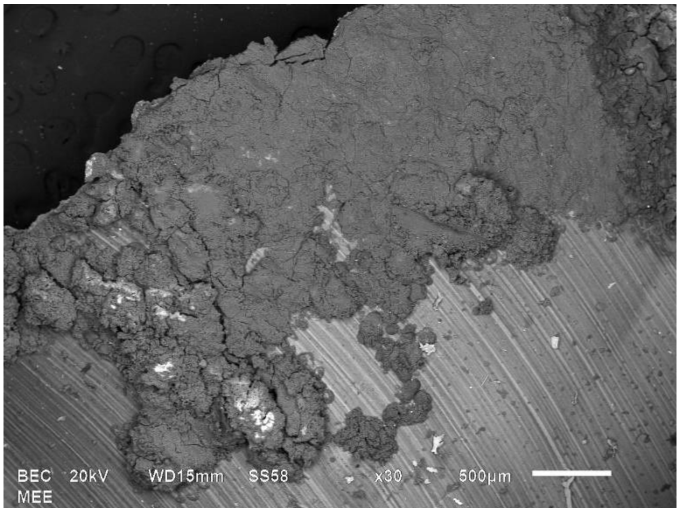

Figure 11 – 30X Corrosion Products on O.D. of Blue Fin Material

Figure 10 shows the beginning of growth of a crystalline material on the inside diameter of the tube.

The corrosion products on the Blue Fin Material, Figure 2, are shown in Figure 11. This is typical of aluminum corrosion.

Energy Dispersive X-Ray Analysis

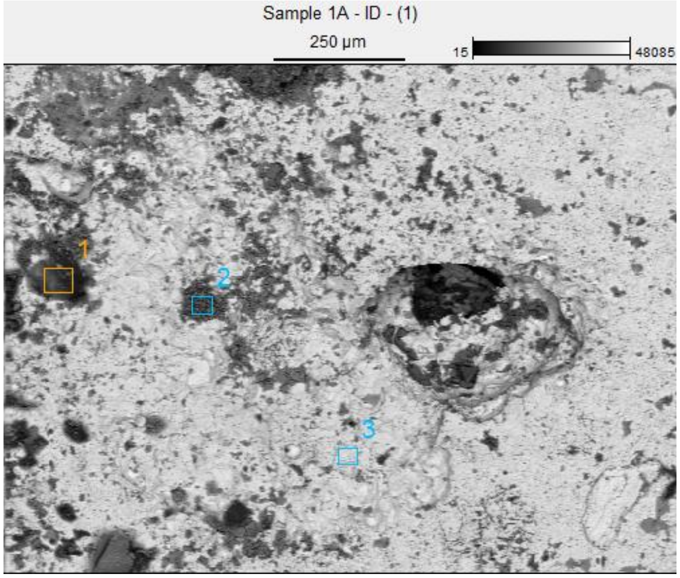

Figure 12 – Spectra Locations near Leak on I.D.

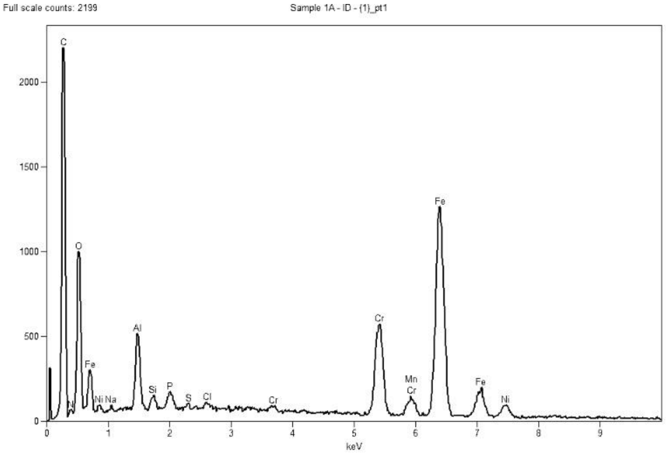

Figure 13 – Spectrum of Location 1 near Leak on I.D.

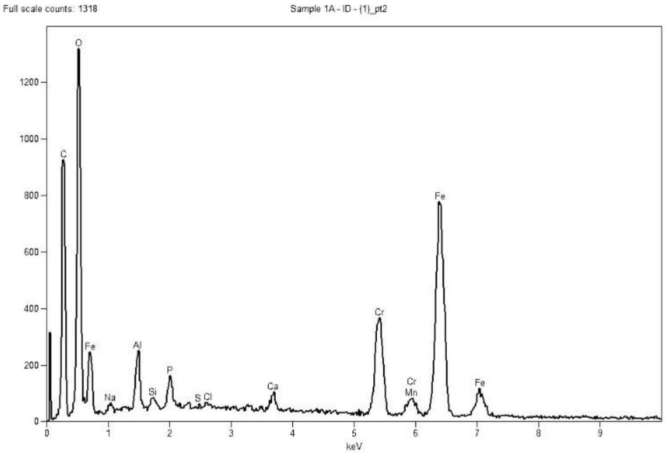

Figure 14 – Spectrum of Location 2 near Leak on I.D.

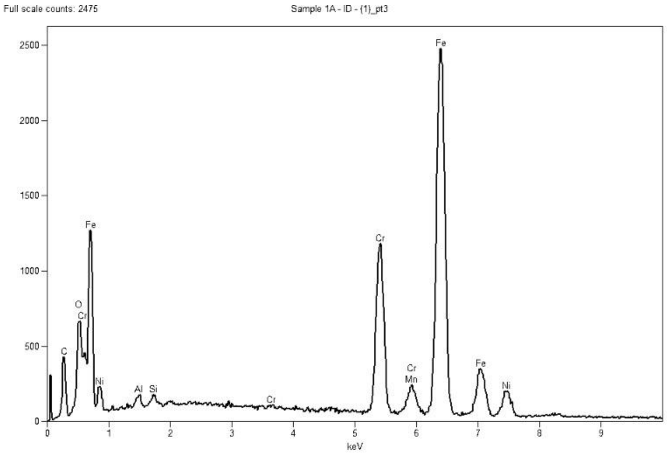

Figure 15 – Spectrum of Location 3 near Leak on I.D.

Figure 12 shows the locations where the debris was associated with the corrosion pit on the inside diameter of the tube. The SEM image was made in the back scatter mode; therefore, the darker material has the lowest atomic weight. Carbon based materials show up as black. The semi-quantitative analysis for the three locations is given in Table 1. The spectra shown in Figure 13 indicates the unusual presence of carbon, sodium, aluminum, phosphorous, sulfur, and chlorine. Chlorine in the form of chlorides is highly corrosive to 304 stainless steel. The spectra shown in Figure 14 indicates the presence of the same unexpected elements, plus calcium. Figure 15 is the spectra for an area of clean 304 stainless steel.

Table 1
Tube I.D. near Leak
(Percent by Weight)

Element/Location	1	2	3
Carbon	25.8	18.1	4.6
Nitrogen	3.4		
Oxygen	18.1	29.4	4.5
Sodium	0.3	0.5	
Aluminum	2.9	2.1	0.6
Silicon	0.4	0.4	0.5
Phosphorous	0.7	1.1	
Sulfur	0.1	0.1	
Chlorine	0.2	0.2	
Calcium		0.6	
Chromium	9.5	10.7	17.7
Manganese	1.0	0.6	1.1
Iron	34.7	36.1	63.8
Nickel	2.9		7.2

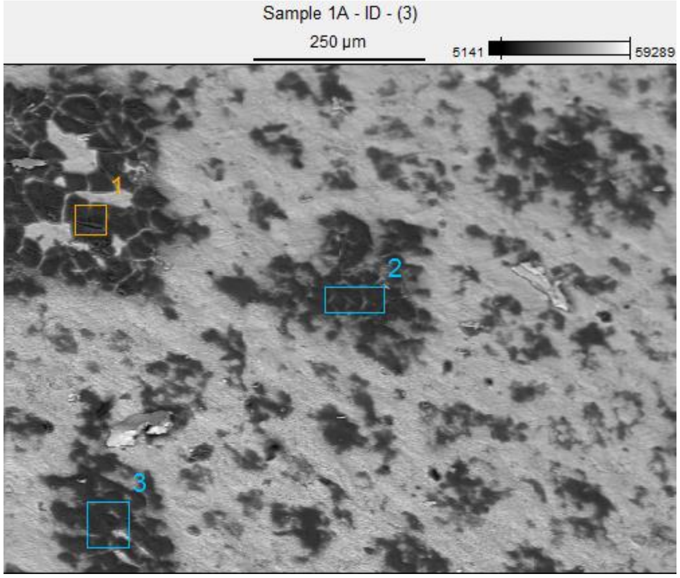

Figure 16 – Spectra Locations for Spots on Tube Wall

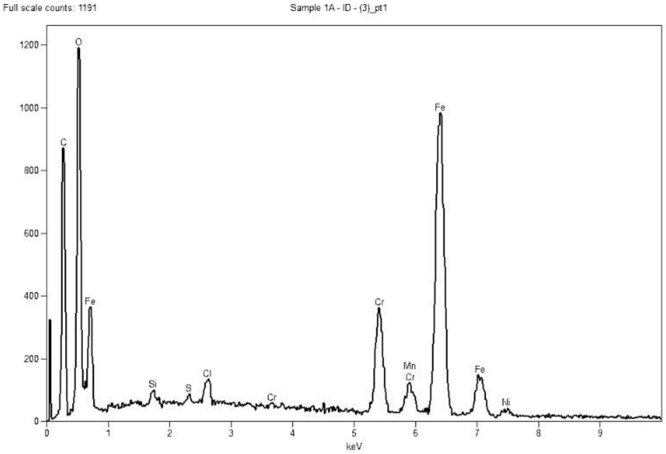

Figure 17 – Spectrum of Location 1 on Tube Wall

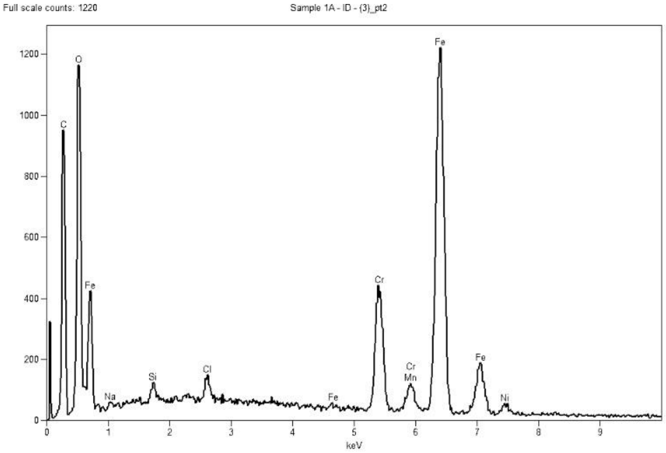

Figure 18 – Sprectrum of Location 2 on Tube Wall

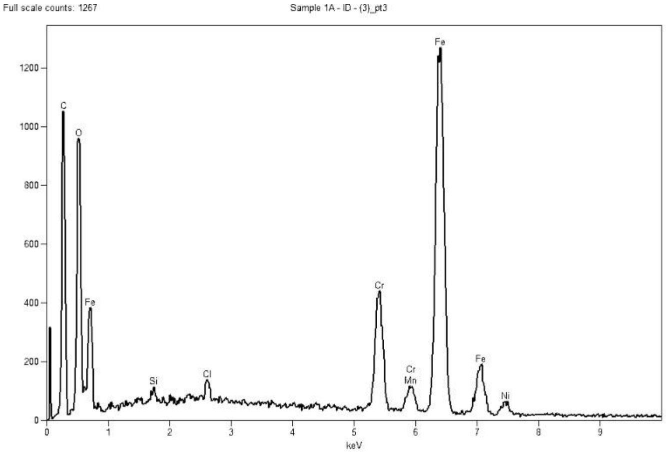

Figure 19 – Spectrum of Location 3 on Tube Wall

The three spots that were analyzed on the tube wall, Figure 16, were virtually identical. The three spectra, shown in Figures 17, 18, and 19, show the presence of iron oxide, organic material, sodium chloride, and stainless steel. The semi-quantitative analysis of these locations is given in Table 2.

Table 2
Spots on I.D. of Tube Wall
(Percent by Weight)

Element/Location	1	2	3
Carbon	16.1	15.8	16.9
Oxygen	24.6	22.1	18.9
Sodium		0.5	
Silicon	0.5	0.6	0.5
Sulfur	0.2		
Chlorine	0.8	0.8	0.6
Chromium	8.8	9.9	9.3
Manganese	2.5	1.6	1.5
Iron	44.9	46.6	50.0
Nickel	1.6	2.1	2.3

The large spot on the inside diameter of the tube, Figure 20, has a spectrum, Figure 21, that indicates that the crystalline material is likely a chlorinated amine salt. The remainder of the spectrum is from the underlying stainless steel.

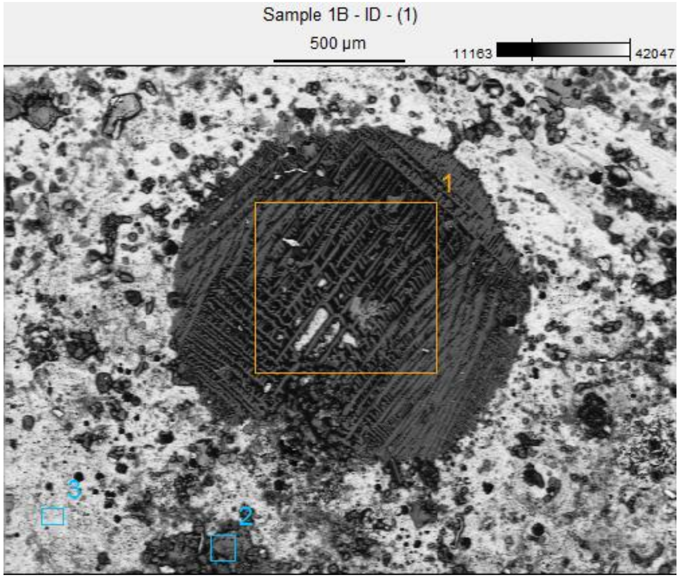

Figure 20 – Spectra Location for Corrosion on Tube Wall

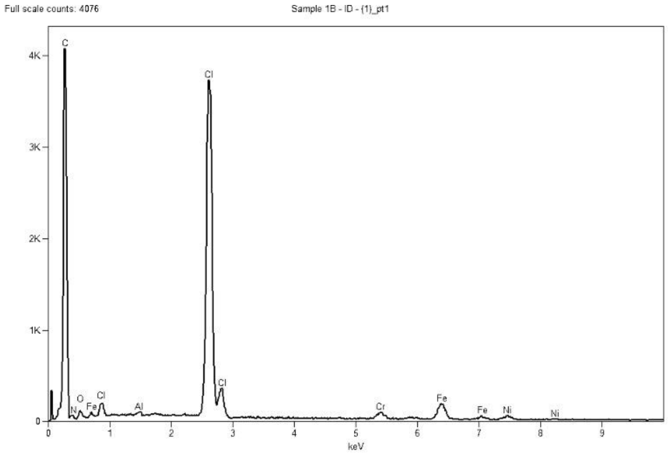

Figure 21 – Spectrum of Location 1 Corrosion on Tube Wall

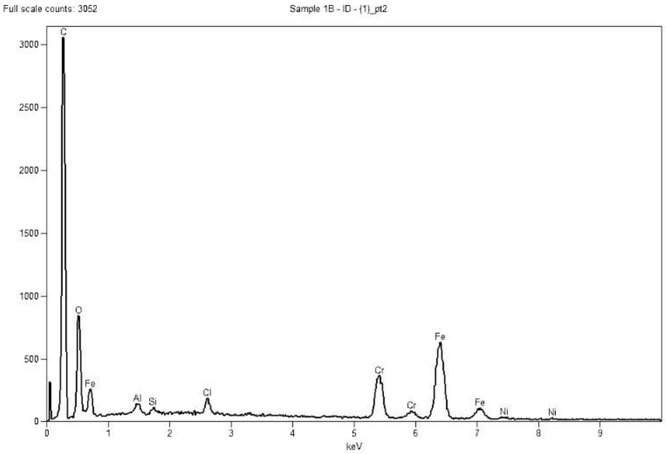

Figure 22 – Spectrum of Location 2 Deposit on Tube Wall

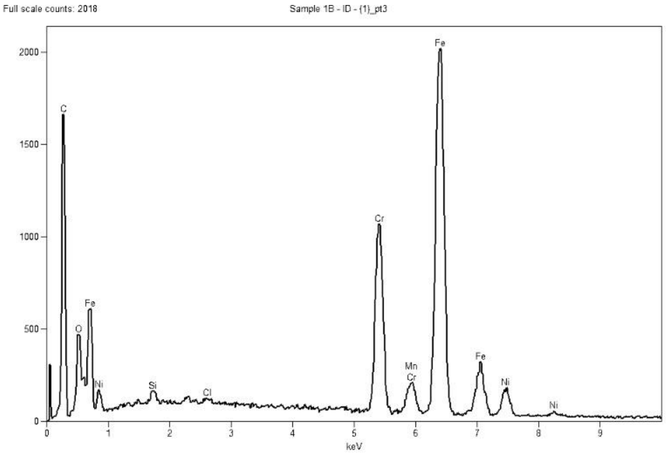

Figure 23 – Spectrum of Location 3 Deposit on Tube Wall

The spot analysis for Location 2, Figure 22, shows organic material, a chloride salt, and underlying stainless steel. Location 3 is similar, but the stainless steel is more prevalent. The semi-quantitative analysis is given in Table 3.

Table 3
Spots on I.D. of Tube Wall
(Percent by Weight)

Element Location	1	2	3
Carbon	64.5	39.3	17.6
Nitrogen	4.2		
Oxygen	1.2	22.3	4.8
Aluminum	0.2	0.9	
Silicon		0.3	0.5
Chlorine	22.1	1.1	0.2
Chromium	1.4	9.0	16.6
Manganese			1.1
Iron	4.9	26.3	53.7
Nickel	1.6	0.8	5.6

The energy dispersive x-ray examination of deposits on the inside of the tube showed that there were chlorides present, which are corrosive to stainless steel, and there were organic materials present. These foreign materials are detrimental to the operation and life of the system.

GCMS

A Gas Chromatograph Mass Spectrograph was used to identify the organic material found on the inside of the tube. The scan of the results is shown in Figure 24. The sample was doped with organic chemicals of a known mass to serve as reference indicators. These chemicals were 1 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12.

The scan indicates that the residual organic material was consistent with mineral oil, diesel oil, and Compressor Oil ISO 68, which is used with liquid ammonia and carbon dioxide systems.

The red/brown color of the residual oxidized oil is due to the presence of iron oxide. Red iron oxide, Fe_3O_4, is a strong oxidizer which would oxidize the oil residue causing it to adhere to the tube inside diameter.

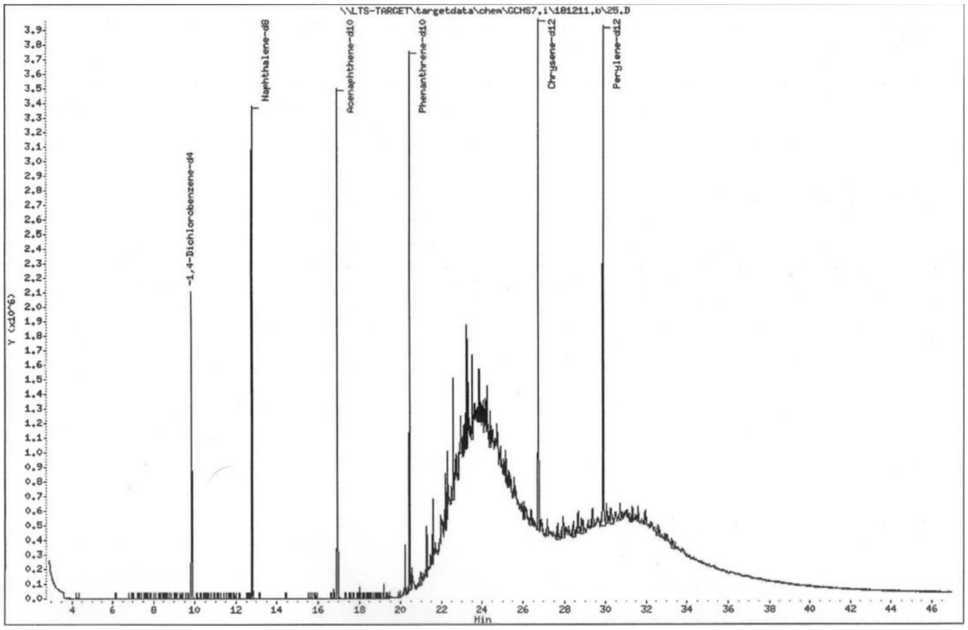

Figure 24 – CGMS Scan for Organic Material in Tube

Metallographic Examination

The samples were electrolytically etched in a saturated solution of oxalic acid to reveal sensitized grain boundaries. This test was done according to ASTM A262 – 15 Practice A. Over the years I have found that Practice A is a far more effective method of determining if austenitic stainless steel has been sensitized. Practice A will detect sensitized grain boundaries that the other ASTM A262 practices will not.

The weld and weld heat affected zones in the tube are shown in Figure 25. The grain boundaries in the heat affected zones were sensitized. Sensitized grain boundaries are caused by heating to between 1000 and 1550 degrees F. The sensitization was the result of formation of chromium carbides in the grain boundary. Chromium carbides have very poor corrosion resistance. The tubing used for this coil was not annealed after welding. Figure 26 shows sensitized grain boundaries.

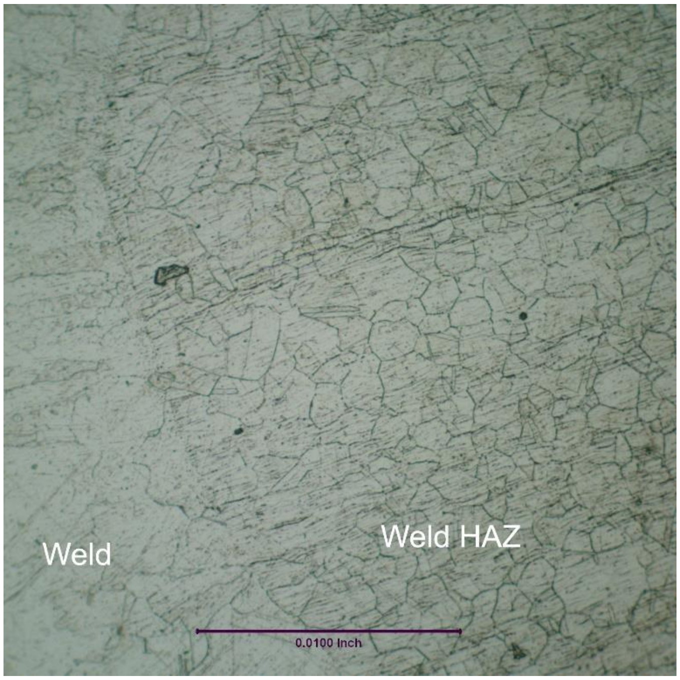

Figure 25 – 200X Weld and Weld HAZ

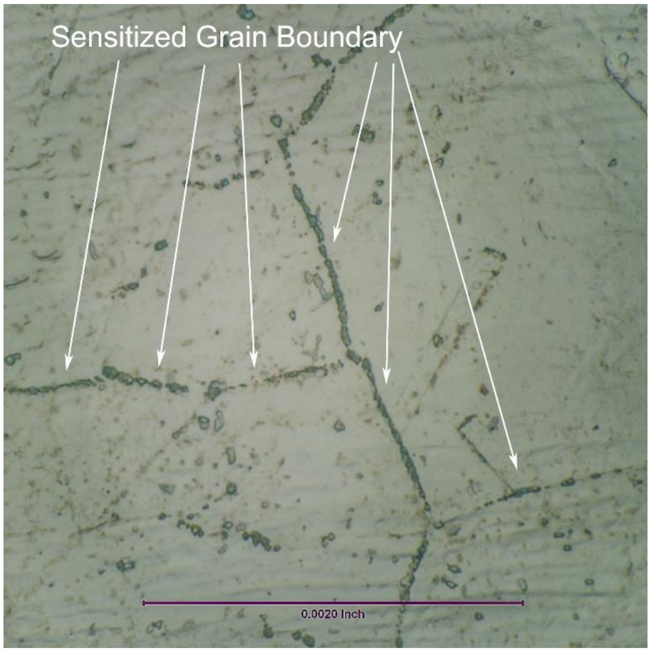

Figure 26 – 1500X Sensitized Grain Boundaries

Discussion

The findings of this investigation show that there was contamination of the ammonia refrigeration system. The contaminates were chlorides, and red/brown iron oxide. Any moisture or oxygen in the system would cause the iron to oxidize and form Fe_3O_4, which in turn can oxidize the lubricant in the system, resulting in the red/brown organic deposits found in the leaking tube. The presence of chlorides in the system would have eventually caused the system to fail. The source of the chlorides was unknown.

The investigation showed that the 304 stainless steel tubing was sensitized, especially in the weld heat affected zone, making the tubing no more corrosion resistant than carbon steel tubing would have been. Sensitization of 304 stainless steel can be avoided by using 304L stainless steel. The tubing was certified by the tubing mill as being free of sensitization using one of the practices other than ASTM 262 Practice A. The sensitized weld heat affected zone was so small that it is not likely that these other practices would have detected the sensitized heat affected zone. Several other coil manufacturers experienced stainless steel coil failures due to sensitization during this time frame with tubing from different tube mills. Both 304 and 304L stainless steel are prone to pitting corrosion in the presence of chlorides and would eventually fail even without having been sensitized.

Conclusions

1) Based on the findings given in this report, the primary causes of failure of this heat exchanger were contamination by chlorides, and sensitized 304 stainless steel tubing.

2) The wrong ASTM A262 Practice was used by the tube mill to certify that the tubing was free of sensitization.