

CORROSION OF ALUMINUM-FIN, COPPER-TUBE HEAT EXCHANGE COILS

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ABSTRACT

Over the past several years the HVAC industry has experienced a large increase in instances of leaks in the central portion of aluminum-finned, copper-tube heat exchange coils. These leaks are characterized as being very small in size and very high in numbers within a single coil. There are many chemical species that can cause these coil leaks, including chlorides from pool chemicals and clothes washing, sulfur from tap water, lubricants and nearby industries, and ammonia compounds from cleaners or nearby industries. However this recent increase in reported coil leaks is being attributed to a newly discovered class of corroding agents. These are low molecular weight organic acids such as acetic acid and formic acid.

This paper gives some background information on leak causes and then presents the diagnostic procedures typically used to determine these causes. Results of some of these analyses are also presented. As many of these procedures are new and often company-specific, there are no accepted industry standard procedures to test process chemicals or application contaminants for copper tube corrosion potential. Industry supported research has begun to develop a bench test for this.

CORROSION DETAILS

Most corroding agents produce relatively straight tunnels through a copper tube wall. This is the more common experience with outdoor heat exchange coils and is usually attributed to galvanic corrosion. This occurs whenever there are dissimilar metals in the presence of water containing an electrolyte. Dissolved salts of chloride are the most common electrolytes. Although, any soluble salt can lead to galvanic corrosion, such as those containing fluoride, bromide, iodide, sulfate, nitrate, borate, etc. When galvanic corrosion occurs, the more sacrificial metal (aluminum in our coils) will preferentially corrode, and by doing so, protect the more noble metal (copper in our coils). Figure 1 shows an outdoor condensing coil that was exposed to a severely contaminated environment. Note the copper tubes are intact but the aluminum fins are gone. This is the image and mechanism that most people think of when considering coil corrosion.

In most failures of indoor coils, however, the copper tubes will have been penetrated while there will be little corrosion on the aluminum fins in direct contact. Figure 2 shows pits in the copper tube surface and the contacting aluminum fin surfaces. In these cases the corrosion appears to be caused by a direct attack of the corroding agent on the copper in spite of the presence of the 'more sacrificial' aluminum. Hydrogen sulfide, carbon disulfide, and ammonia have been known for centuries to cause copper corrosion without the presence of a conductive electrolyte solution or a 'more noble' metal. The capability of low molecular weight organic acids to directly attack copper and produce leaks in heat exchange coils is new knowledge to the HVAC industry. This is not to say that it is new to chemistry, or that chemists in the HVAC industry somehow lacked this important information, but that it was never understood to be a cause for actual leaks. In fact acetic acid has been used for centuries to treat copper by mild, uniform surface attack. What is unexpected is that this attack will concentrate in specific places and penetrate the tube wall, rather than just uniformly etch the tube surface.

Leaks caused by organic acids typically appear as a single initiation hole that branch into several tunnels of which only one or a few actually penetrate the entire tube wall. As these tunnels appear similar to those in an ant colony, they are often referred to as 'formicary' corrosion. Figure 3 shows microscopic images of the cross section of two copper tubes showing this phenomenon – one starting from the inside and one from the outside.

Thus for these indoor coil leaks, the corroding agents are different, and they penetrate the copper tube by a different mechanism than typically seen with outdoor coil corrosion. It should be noted that the segregation of these two corrosion mechanisms between outdoor and indoor coils is not perfect. Most instances of formicary corrosion have been reported for indoor coils, with far fewer reported for outdoor coils.

CORROSION ANALYSIS PROCEDURES

Knowing all of this, how does one determine the cause of leak formation in these coils? There are probably as many different approaches to this as there are people doing them. Presented here is a collection of procedures used in the industry. The

order of the procedures is such that if one elected to use them all, performance of one test would not interfere with that for subsequent steps.

- 1) Confirm that the coil actually has leaks and pinpoint leak locations.
- 2) Remove fins to reveal bare tubes at leak locations.
- 3) Examine tubes under microscope.
- 4) Rinse coil with distilled/de-ionized water and analyze for anions.
- 5) Perform elemental analyses on leak sites.
- 6) Try to put two-and-two together.

Below is a closer look at each of these procedures and what can be learned from the results.

1) Leak Confirmation

There is nothing more frustrating than trying to find leak causes on a coil that never had a leak or had one caused by a manufacturing defect. Defects in tube welding, and in tube processing can produce leaks at any position in the coil. These kinds of failures are suspected when only one leak is found in the coil, or found in only one U-bend. The general appearance of the coil can reveal candidate causes. For instance, a coil with black copper tubing and clean shiny aluminum has likely been attacked by sulfur. The next steps would be confirmation of sulfur. Figure 4 shows copper tubes with typical black sooty appearance of sulfur attack.

Pinpointing the leak location(s) is important for later analyses. Leak location can provide evidence of the corroding agent source. Figure 5 shows internal tube corrosion in a coil. The corrosion was only present in the first tube in each circuit. This indicated that the corroding agent was not from the coil itself, but from somewhere upstream. Leaks that occur in only the bottom row of the coil are likely to be caused by some corroding agent in the condensate water, if not by some physical defect. High chlorine was found in the bottom row of one coil returned from a home. A little diplomatic questioning revealed that the homeowner had been pouring chlorine bleach in the drain pan to kill ‘bugs’ growing in there!

2) Fin Removal

This is a laborious exercise that requires a lot of persistence. The intent is to reveal the leak location in the copper tube for further analysis. The Japanese copper tubing manufacturers seem to have perfected a technique for an entire coil as shown in Figure 6. It works relatively well on 1-row and 2-row coils, but poorly on deeper coils. The steps are slitting the fins along the tubes, twisting/tearing the fins, and finally pulling the fins out. The picture on the right shows the typical purple to black color of formicary

corrosion on the upper rows and little corrosion on the bottom rows. This followed the airflow pattern for this coil, indicating the corroding agent was likely from the application environment.

3) Microscopic Examination

With the fins off and the tube surface exposed, microscopic examination is possible. If the tube in the area of the leak is clean and no pitting is observed, it may indicate that the leak initiated from the inside. Slitting the tube and spreading it open would reveal darkened inside surfaces and pitting in these cases. Most often though, the exterior will resemble a lunar landscape – pockmarked with pits. Often times these areas also show salt deposits. Analyses of these deposits can sometimes reveal the corrosion cause. Figure 7 shows microscope images of several pitted tubes. The vertical stripes are caused by the contact of the aluminum fins. The light-color copper bands are where the fin collars touched the copper tube. The darker gray or black bands are the spaces between the fins. It is in these bands between the fins that pitting is predominant. The edge of the fin collar creates a miniature crevice in which corroding agents can concentrate during drying cycles and thus focus their strength in one spot creating a pit, rather than general surface corrosion.

4) Coil Rinsing and Anion Analysis

This step is most difficult, as the coils are large and the water must be very pure for any real benefit. In addition, few labs have Ion Chromatography capability and many of those are not calibrated for this kind of analysis. The intent is to collect and identify the negative ions (anions) that are on the coil. These anions include many of the active species that directly attack copper, such as chloride, fluoride, bromide, iodide, sulfate, nitrate, acetate, formate, and other soluble low molecular weight organic anions. It should be noted that a coil that has been submerged in tap water to confirm leaks, will not be suitable for this test, as this water submersion will remove some of the anions of interest as well as add others (chloride, fluoride, sulfate) that are commonly present in tap water.

The very best way to obtain a representative water sample for Ion Chromatography is to collect the condensed water from the coil while in operation. If this cannot be done, coil rinsing is the second choice. One problem with analysis of condensate or rinse water is in the case where there was a single contamination event in which leaks developed but were not discovered for a long time. The long time after the event may be sufficient for the corroding anion to be completely rinsed from the coil – erasing

the evidence. An example of this is domestic canning. Canning pickles in the summer will release high concentrations of acetic acid in the air that condense on the air conditioner coil. This can lead to formicary corrosion in the coil which will likely not to be diagnosed until the following year, at which time evidence of the acetic acid is long gone.

Figure 8 shows two ion chromatograms for air conditioner condensate samples from two homes. In Sample A the condensate contained high levels of sulfate, and the condensate in sample 3 contained both acetate and formate indicating formicary corrosion.

5) Elemental Analyses of Leak Sites

The Scanning Electron Microscope (SEM) has proven to be a very valuable tool for analyzing leak sites from HVAC coils. First, detailed photographs can be made at very high magnification that show the topography around the leak site. Figure 3, mentioned above, shows SEM photos of tubing cross sections at 200X magnification. Then using the Energy Dispersive X-ray (EDX) feature on the machine, the elemental content of the feature can be obtained. Figure 9 shows an SEM image of a contaminated tube surface and the EDX analysis of the salt on the surface. With careful sample preparation, the elemental composition in the bottom of a pit can also be determined. Analysis of these pit contents can be very valuable in sorting out the responsible corroding agent when there are multiple contaminants on the tube surface. Figure 10 is an image of a typical corrosion pit with the associated EDX elemental analysis of the bottom of that pit. Note the increase in silicon in the pit as compared with the surface analysis in Figure 9. Silicic acid has been implicated in some coil leak instances.

One problem with SEM and EDX analyses is that they are conducted on samples under vacuum. If the corroding agent is volatile – as is the case with formicary corrosion caused by acetic or formic acid – then the vacuum will remove most, if not all, of the critical evidence. Figure 11 is an EDX analysis of a typical formicary corrosion pit. One would expect to see the elements from the acid – carbon, oxygen and hydrogen. Only oxygen is found in the analysis. The hydrogen cannot be detected by EDX anyway, and the carbon is gone. Oxygen is present as oxides of

copper. The current theory on formicary corrosion includes formation of copper oxide as a necessary step.

6) Putting it together

The first step is “Round up the usual suspects!”, and the next step is to sort the guilty from the innocent. It is in this last step where all of this can be useful. As mentioned before, it is not likely that all of these procedures will be necessary. If the copper tubing looks like it has been in a sooty fire, just skip to SEM/EDX to confirm sulfur as shown in Figure 12, or use a wet chemical procedure for copper sulfide. If a likely cause of corrosion cannot be surmised from the visual appearance of the coil, then start going through the steps one at a time until some condemning evidence is obtained. The costs for the first few steps are lower than those for the last steps. In-house visual examinations, coil tear-down, and microscopic examinations can be performed with little expense prior to obtaining the more costly outside analyses by Ion Chromatography or Scanning Electron Microscopy. It does happen in some cases that the cause cannot be determined, but in every case many potential causes can be eliminated.

INDUSTRY STATUS

There are a couple conflicting theories in the industry concerning the mechanism for formicary corrosion. There have been many papers written on the subject with most of these from the copper producers in Japan. The Air Conditioning, Refrigeration Technology Institute has initiated a project under its 21-CR program to determine the actual mechanism involved, and from this develop a bench test that produces formicary corrosion in copper tubes when subjected to the necessary corroding agents and environmental conditions. Success in this project will give the industry the ability to assess potential corroding agents and their sources as well as develop remedies against this form of attack.

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Figure 1. Outdoor Coil showing evidence of galvanic corrosion.



Figure 2. Corroded copper tube and adjacent aluminum fins.



Figure 3. Cross sections of copper tubes with formicary corrosion initiating from the inner wall (left) and outer wall (right).

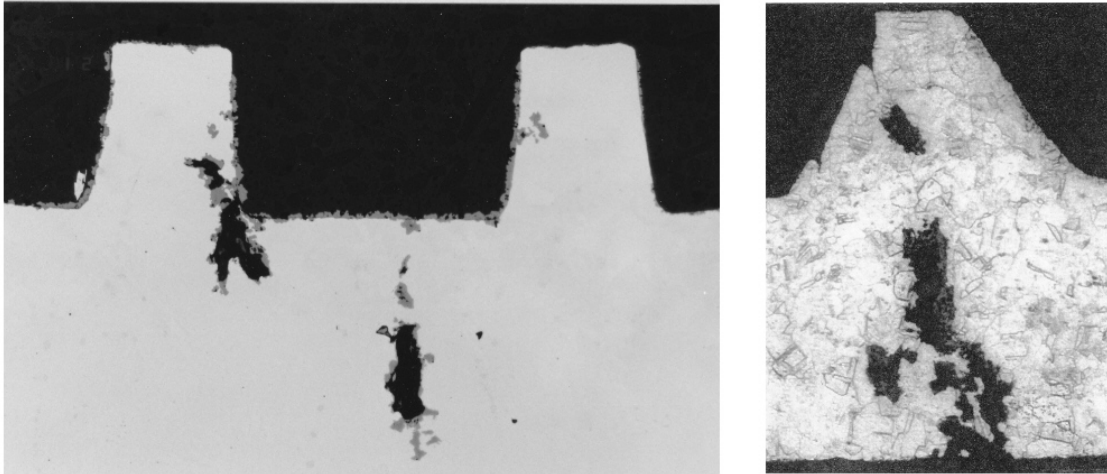


Figure 4. Appearance of sulfur attack on copper tubes.



Figure 5. Interior surface of corroded copper tube at capillary inlet end (left) of circuit and at suction manifold end (right) of circuit.



Figure 6. Two row coil with fins cut and twisted (left) and completely removed (right). Note blue-black color typical of formicary corrosion.

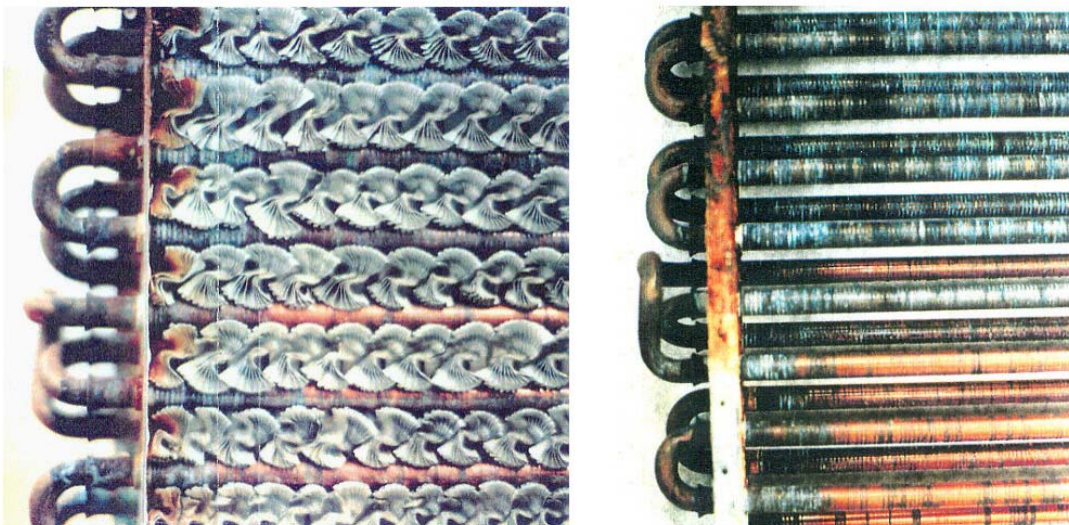


Figure 7. Microscope images of pits in copper tubing. (60X Magnification)

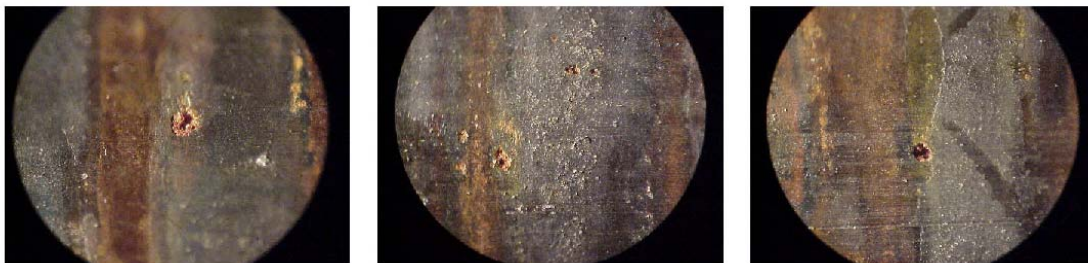


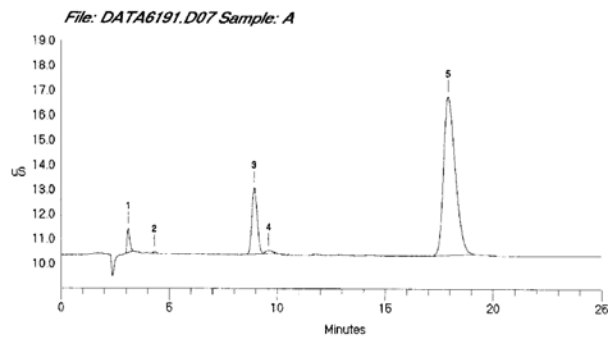
Figure 8. Ion chromatograms for condensate from two coils. One with high sulfate (top) and one with acetate and formate (bottom).

***** Component Report: Components Found *****

Pk. Num	Ret Time	Component Name	Concentration ppm	Height	Area	Bl. Code	%Delta
1	3.09	Fluoride	0.256	9789	87755	1	0.98
2	4.30	Pentanoate	0.469	653	6556	1	-4.37
3	8.92	Chloride	2.017	26813	464045	2	0.26
4	9.60	Heptanoate	3.146	1380	30893	2	-1.81
5	17.91	Sulfate	21.163	64030	2425785	1	-3.71
Totals			27.051	102665	3015034		

***** Peak Report: Unknown Peaks *****

Pk. Num	Ret Time	Component Name	Concentration ppm	Height	Area	Bl. Code	%Delta
Totals			0.000	0	0		



***** Component Report: Components Found *****

Pk. Num	Ret Time	Component Name	Concentration ppm	Height	Area	Bl. Code	%Delta
1	3.32	Acetate	55.351	111871	1495060	1	-0.40
2	3.86	Formate	30.920	215347	2564093	1	-0.43
3	6.18	Hexanoate	1.680	1410	23059	1	0.27
4	8.42	Chloride	1.779	22150	409217	1	0.68
6	17.02	Sulfate	0.649	2110	74395	1	-0.78
Totals			90.378	352888	4565824		

***** Peak Report: Unknown Peaks *****

Pk. Num	Ret Time	Component Name	Concentration ppm	Height	Area	Bl. Code	%Delta
5	10.99		0.000	899	15129	1	
Totals			0.000	899	15129		

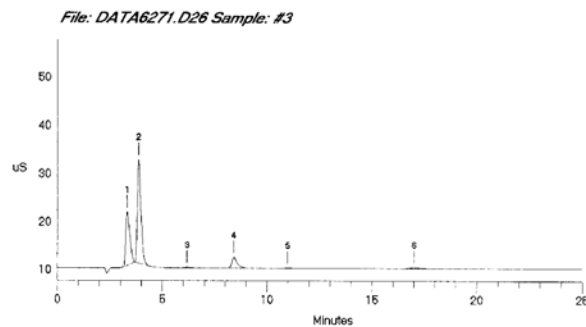


Figure 9. SEM photo and EDX analysis of salt deposits on copper tube showing presence of oxides of aluminum and copper.

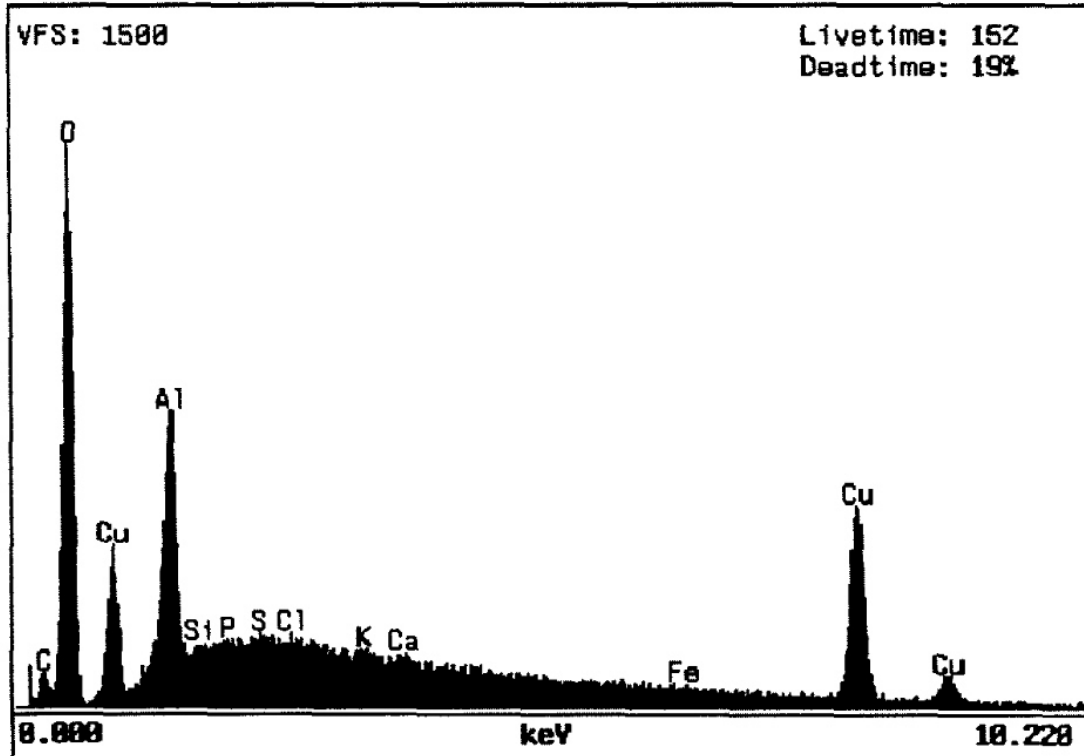
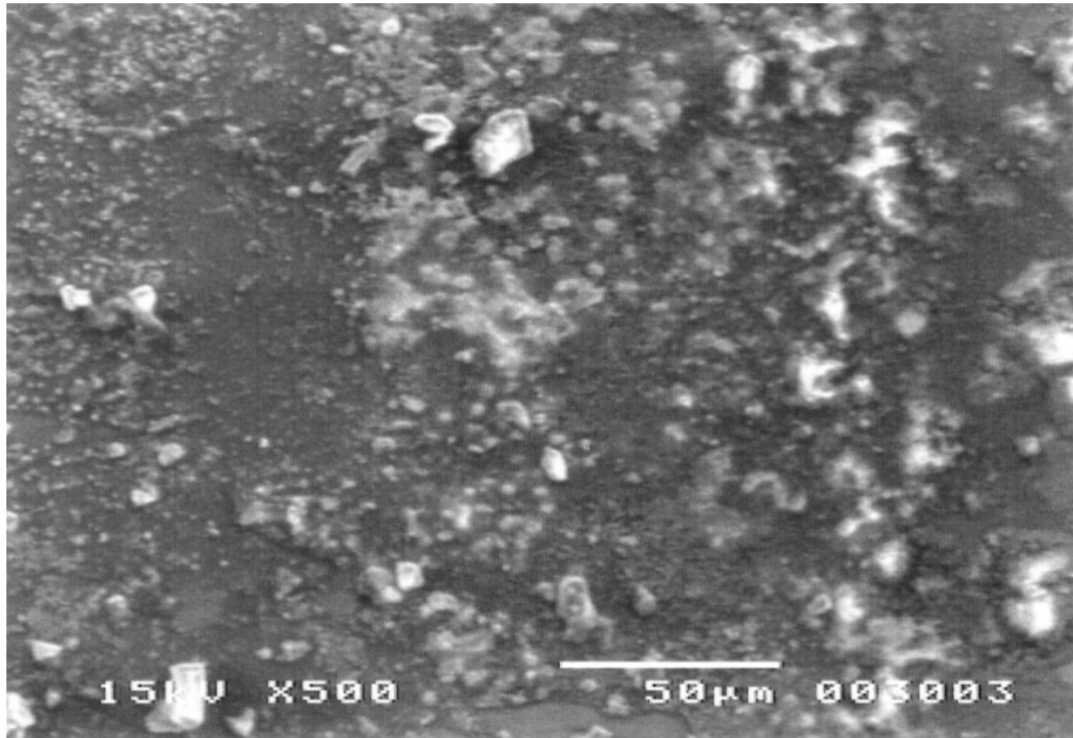


Figure 10. SEM photo and EDX analysis of a pit bottom in a copper tube. The analysis reveals the presence of silicon in the pit.

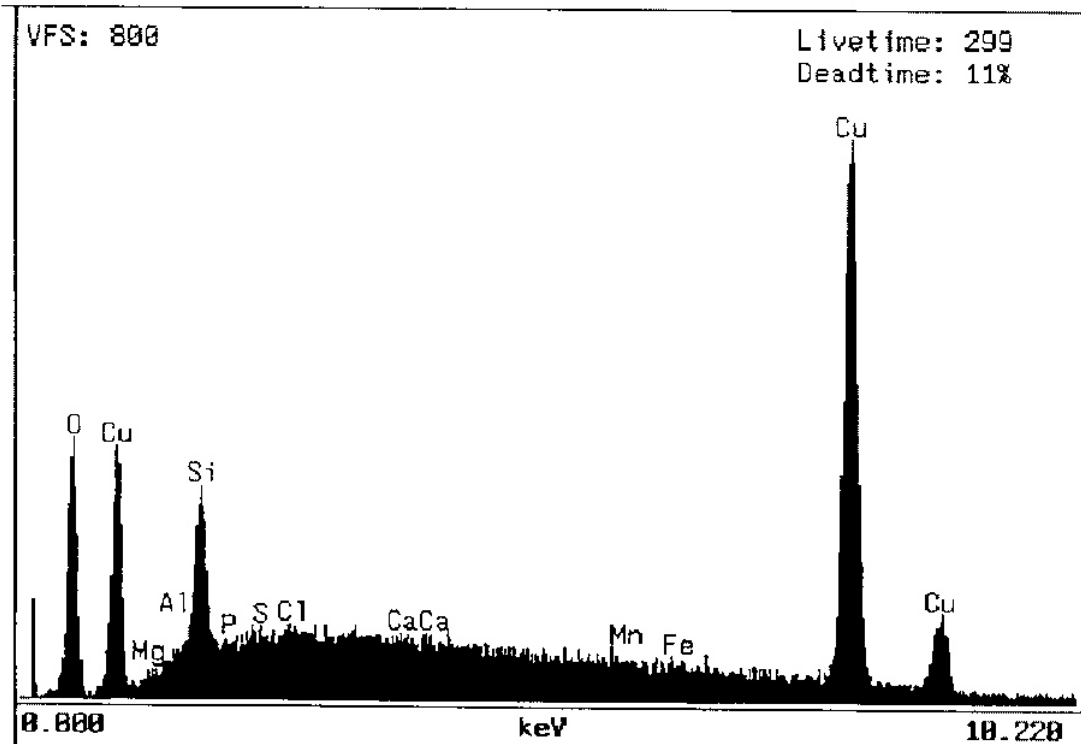
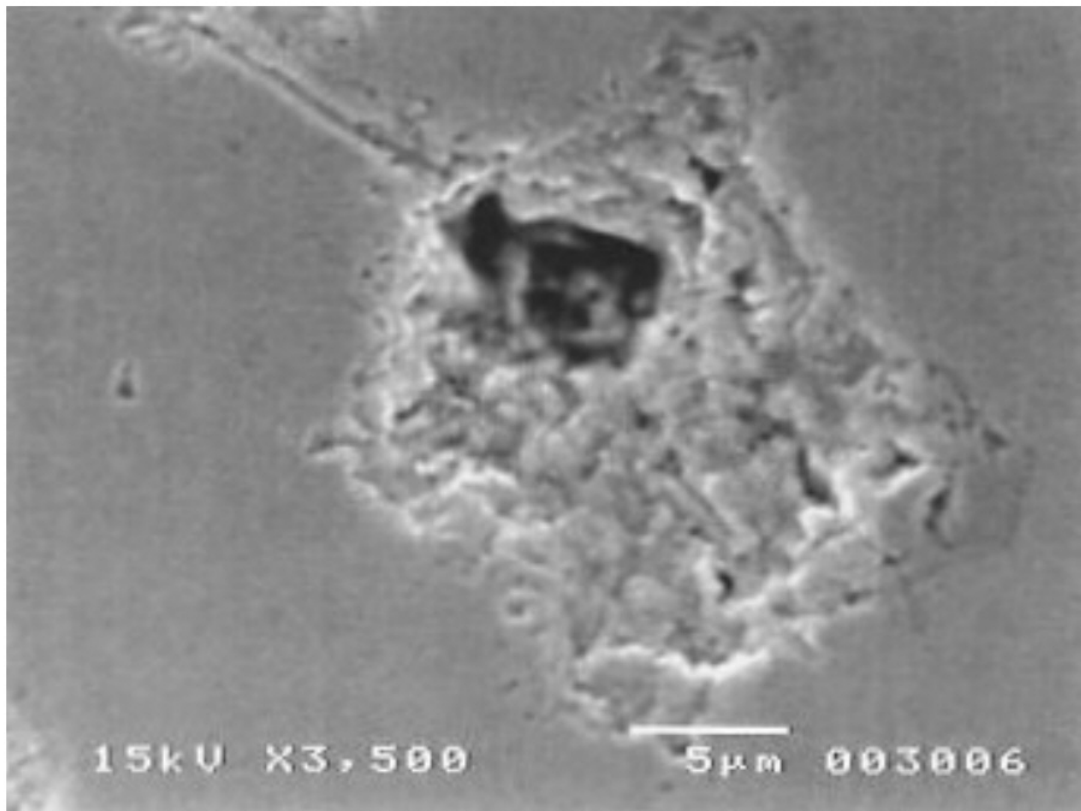


Figure 11. SEM/EDX analysis of a formicary corrosion pit showing only copper and oxygen.

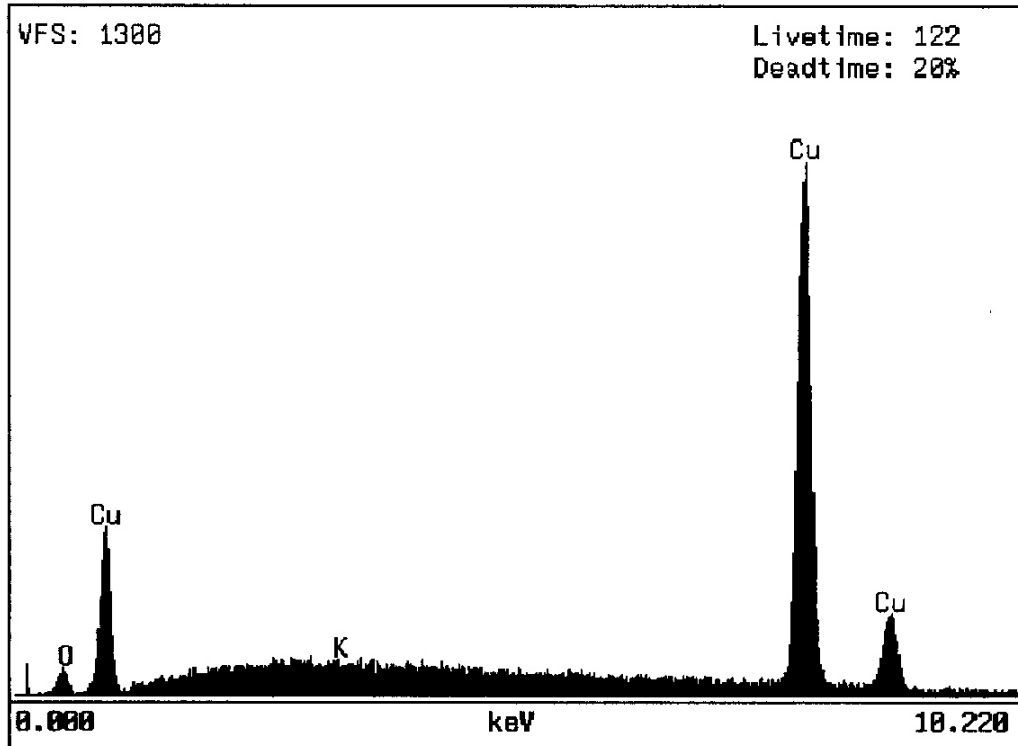


Figure 12. SEM/EDX analysis of copper tubing surface showing presence of sulfur.

