the Conduit

A quarterly publication from
M&M Engineering Associates, Inc.

Vol. 14, No. 1

INSIDE THIS ISSUE:

Investigation: Water Cooled Generator Stator Bars

By: Karen Fuentes
Sr. Principal Engineer

M&M Engineering Associates, Inc. has been involved in the investigation of issues with water cooled generator stator bars beginning with the investigation of the viability of in-place repair of leaking water boxes in the 1990s. More recently M&M Engineering investigated the cause of restrictions and plugging of stator cooling passages which had undergone a water box repair procedure.

Two generator stator bars (A and B), removed from a General Electric (GE) water-cooled generator, were received for examination. Reportedly, the bars contained plugged or restricted cooling passages, resulting in hot spots in the generator stator. The water boxes on the generator had been repaired using the epoxy technique. There was some concern that over time the epoxy had begun to spall and the spalled epoxy was causing blockage or plugging of the copper cooling strands.

Conclusions

Copper oxide deposits caused the plugging and restrictions of the cooling strands. It was concluded that the epoxy used to repair the ends of the stator bar strands within the water box did not contribute to the formation of the restrictions and plugs, and neither did inappropriate water chemistry control as only copper was observed in the deposits (oxides) causing the blockages and restrictions. Additionally, the oxides found are formed under elevated dissolved oxygen conditions; the unit from which the samples were removed has stator cooling water that is controlled to operate with elevated dissolved oxygen levels.

Findings

- Deposits resulting in restriction and plugging of the strands were due to the formation of copper oxide CuO (tenorite) that forms in oxygen-rich environments. The unit is operated with elevated dissolved oxygen.
  - The restricted or plugged strands were on the outside of the stator bundle.
  - Oxide were observed throughout the length of the strands, but restrictions and plugs were more common near the ends of the strands at bends.
  - Oxide formation appears to be influenced by flow (“wing” formation).
  - Oxides appeared to be accumulating/growing into the

fluid stream (away from the wall) rather than along the wall.

  - Three morphologies of oxide were observed.
    - Thin layer along the surface, some with rosette-type appearance.
    - Coral-like, thicker layer extending into the cooling water stream.
    - Feathered, thicker layer extending into the cooling water stream.
  - Morphologies appeared layered suggesting different morphologies were formed under different conditions.
- Pitting of the strand surface was observed under the copper oxide.
  - Generally pits were aligned with voids in the surface deposits.
  - Pits appeared round bottomed with little undercutting.
- The epoxy used to seal the faces of the water boxes did not contribute to the plugging or restrictions.

Identification of Restrictions

The exact location of the restrictions and plugs were not known so testing was required to identify their general location. The bars were sectioned to allow testing to be performed. The water boxes were cut from each end of each bar, the curved section of the bar was cut from each end of each bar, and the straight section of each bar was cut into multiple lengths. A manifold was cast and fit on the end of each stator bar test section so that gas flow could be uniformly introduced across the face of the stator bar cooling passages. Air of a known pressure was introduced at one end of the bar and the air velocity at the opposite end of the bar was measure using a hot wire anemometer. Each cooling strand was checked individually for air velocity. This method proved to accurately detect both plugged and restricted cooling strands. As some of the stator cooling strands wrap around the bar bundle, the location of each cooling strand was verified on each end of each test section using an ohm meter to check the electrical conductivity of each strand.

The air velocity testing showed that there was one identifiable restriction in the straight central section of stator Bar A. The most severe restrictions and plugged strands were identified in the turbine ends of both stator bars. However, some restrictions were also identified on the collector ends of both stator bars, but no plugged strands were identified. In total, seven cooling strands were identified as either plugged or with restrictions; three in stator Bar A and four in Bar B.

The stator bar sections containing restrictions and plugs were initially X-ray radiographed in the assembled condition to try to determine the location of the restriction and plugging. However, because of the stacking of the cooling strands, specific areas of blockage could not be discerned in the radiographs. The stator bar sections were sectioned further and the shorter lengths were re-tested using the air velocity method. Once the section was reduced to approximately one foot or less in length, the cooling strand with the plug or restriction was marked and the stator bar section was disassembled and the cooling strand removed from the bulk of the stator bar section. The individual cooling strands were then radiographed to identify the specific location of the plug or restriction (Figure 1 and Figure 2).

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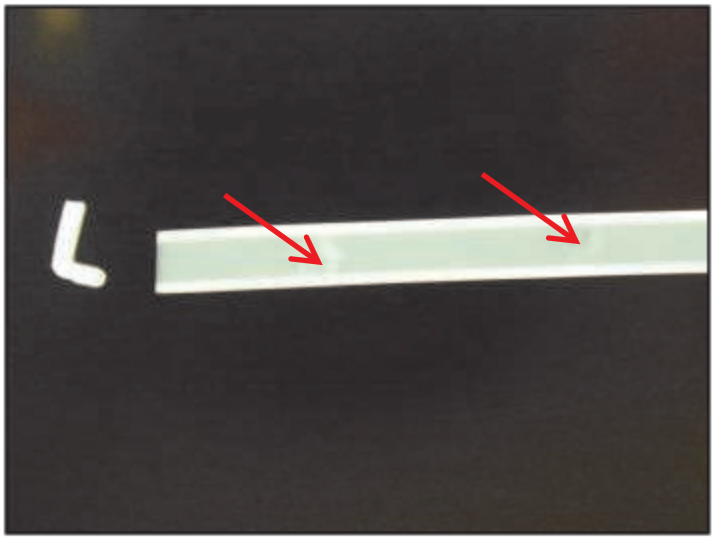

Figure 1.

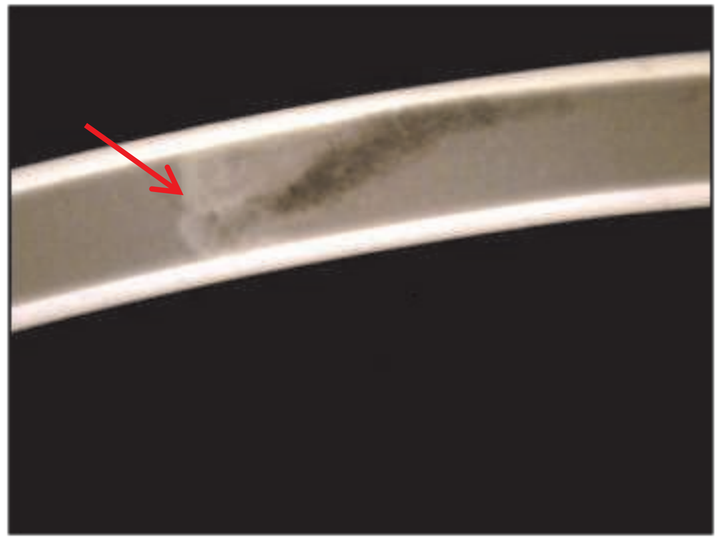

Figure 2.

Sample Preparation

Multiple samples were removed from the areas with identified plugs and restrictions. Additionally, samples were removed from areas immediately upstream and downstream of the plugged areas, as well as from the long straight run with no indications of restrictions or plugs.

Upon initial sectioning, the internal condition of the strands with the plugs was visually examined and photographically documented. The deposits were observed extending from the inner walls of the strands (Figure 3) and in some cases completely plugged the internal passage. The deposits were dark grey to black in appearance.

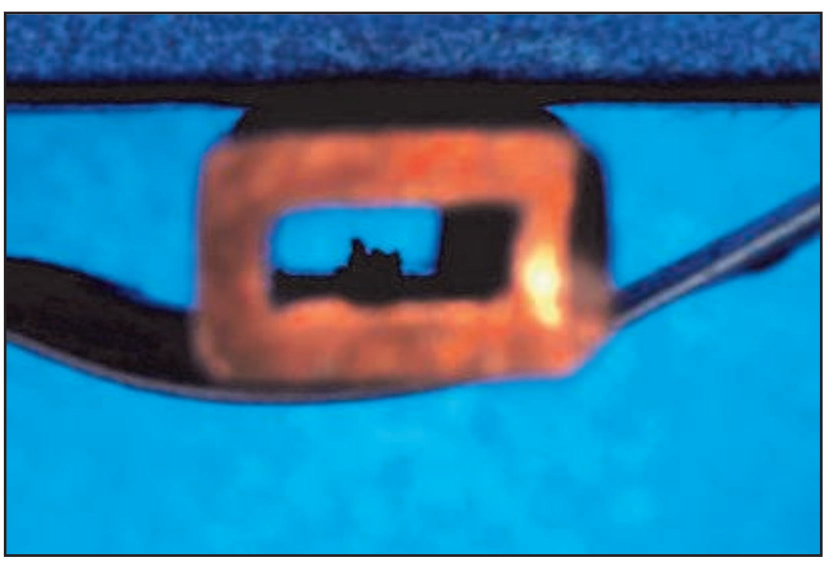

Figure 3.

The strands were then prepared so the cooling channels could be opened for examination of the internal surfaces. The ends of the strand samples were crimped to prevent the mounting resin from entering the strand. The samples were then mounted in resin and ground, leaving a paper-thin remaining wall thickness. The remaining wall was then carefully removed to reveal the internal strand surfaces. The deposits were chemically analyzed *in situ* and once completed, the metallographic preparation was continued. One of the opened strands was filled with epoxy to encapsulate the deposits and the sample was prepared for metallographic examination using standard laboratory techniques of grinding and polishing.

Metallographic Examination

A sample from a straight section of the stator bar was found to contain a bend when the strand was removed from the bar. It contained a buildup of deposits. Examination of the internal strand wall showed that there was pitting under the

Figure 4.

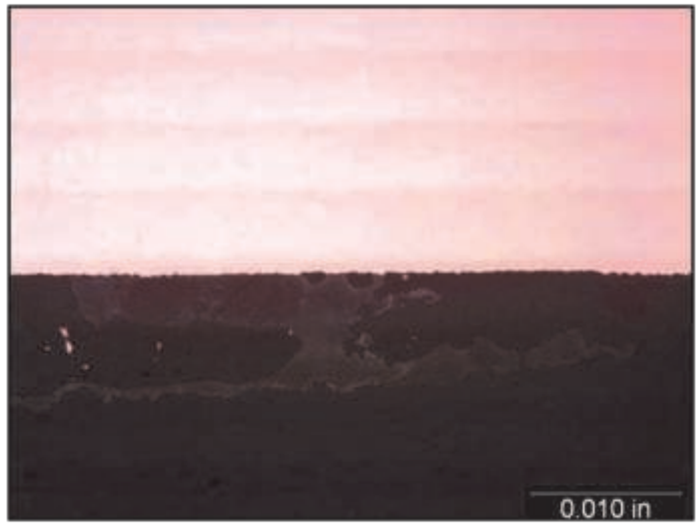

Figure 5.

deposit build-up (Figure 4). The pit bottoms were uneven and appeared deepest under the thickest deposits.

The section of the strand prepared downstream of the build-up contained a thin even layer of deposits. No pits similar to those observed along the internal strand walls of the sample in the plugged area were observed. The appearance of the internal strand wall was slightly different in areas where there were voids in the deposit at the strand wall, as compared to areas in which the deposit was in contact with the strand wall (Figure 5).

The sample prepared upstream of the plugged area had no deposit or pitting similar to that observed along the internal strand walls of the downstream sample.

Over a dozen other samples from restricted and plugged areas as well as areas immediately upstream and downstream of restrictions or plugs and in the straight section of the bar with no indications of restrictions or plugs were examined with similar results.

SEM Examination

The morphology of the material building up and plugging the strands was documented at various magnifications in a scanning electron microscope (SEM). Three morphologies of oxide were observed (Figure 6): feathered, thicker layer

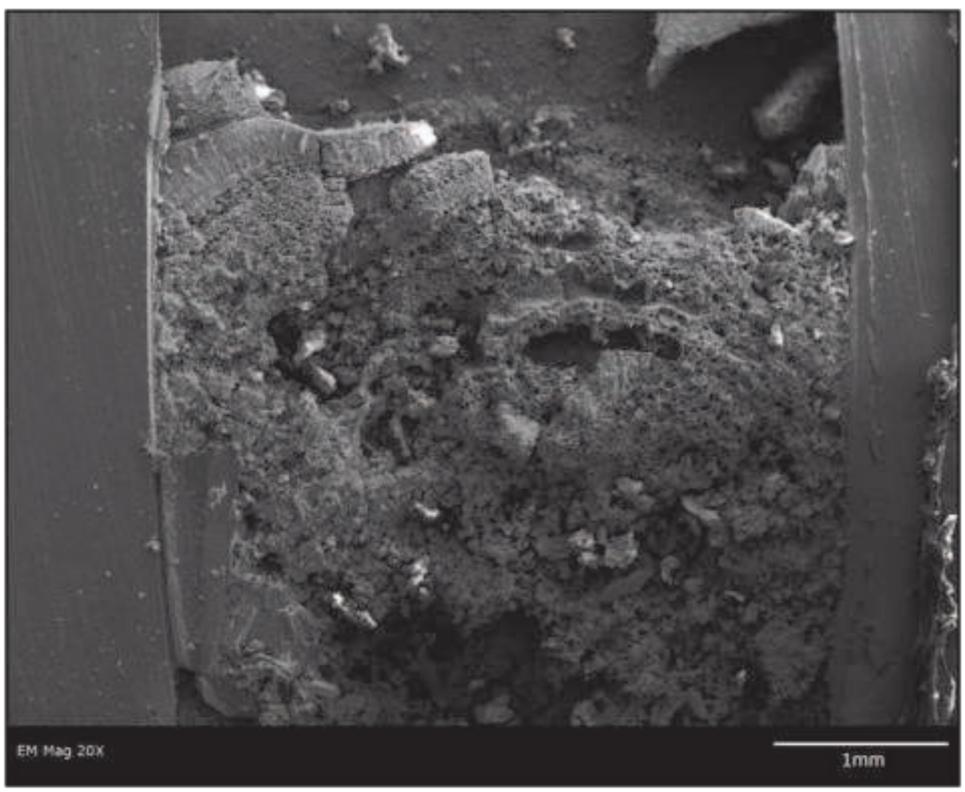

Figure 6.

(Continued from page 4)

extending into the cooling water stream (Figure 7), coral-like, thicker layer extending into the cooling water stream (Figure 8), and thin layer along the surface, some with rosette-like appearance (Figure 9). The layering suggests that different morphologies were formed at different times or under different conditions.

Examination of the strand walls on the sample removed from the straight section of the bar with no indications of restrictions or plugging had a pocked appearance (Figure 10).

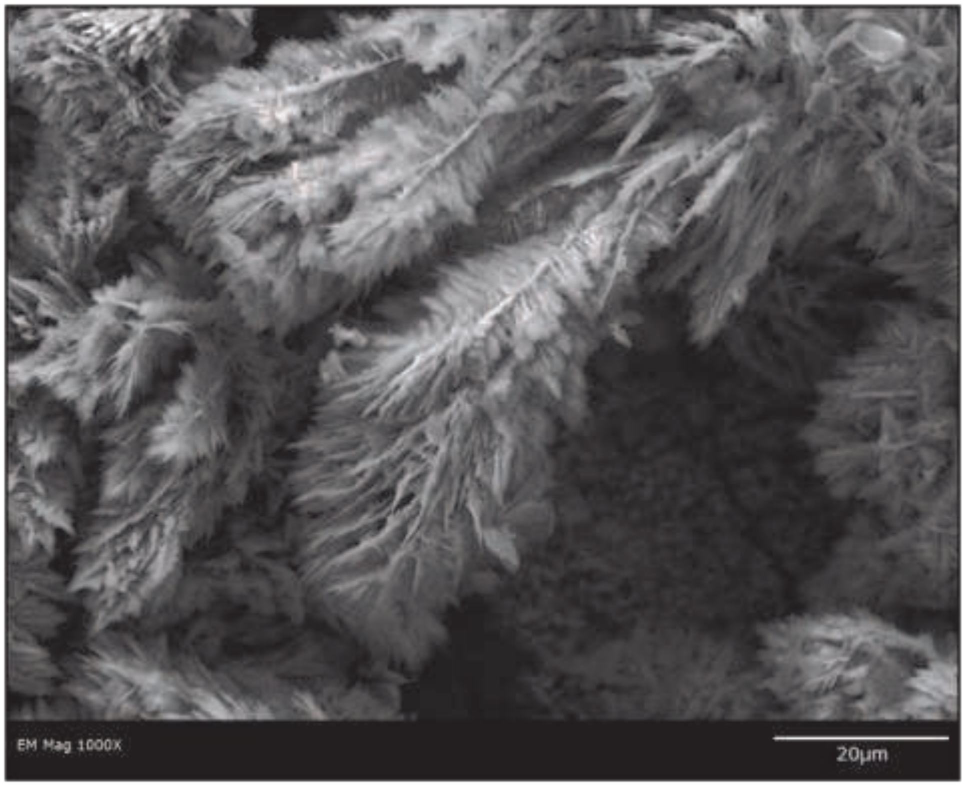

Figure 7.

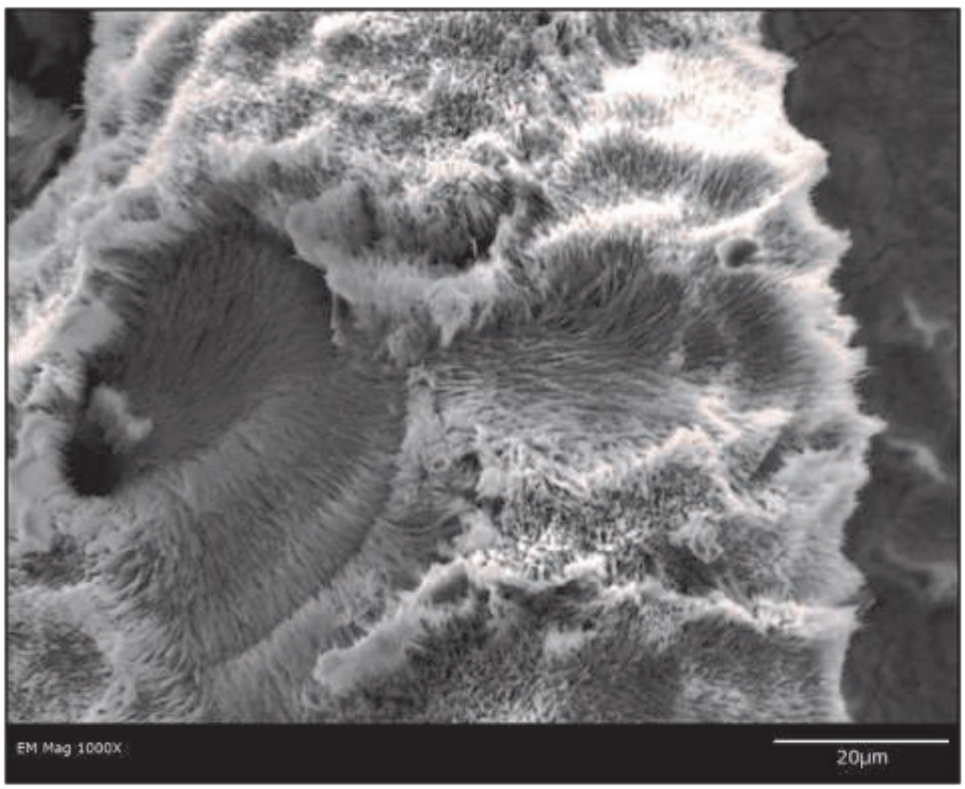

Figure 8.

In Situ Micro-XRD Analysis

The deposits in the opened sections of Bar A strands were analyzed to determine the compounds present in the deposits. A general analysis of a plugged area was performed and then specific areas containing the deposits with the three observed morphologies (thick and feathery, thick and coral-like and thin with some displaying a rosette-like appearance) were analyzed. All areas analyzed were found to contain tenorite (CuO), a form of copper oxide typically found in environments with elevated dissolved oxygen.

Water Box Visual Examination

The internal conditions of the water boxes, strand ends and epoxy repairs were visually examined and photographically documented. The strands and

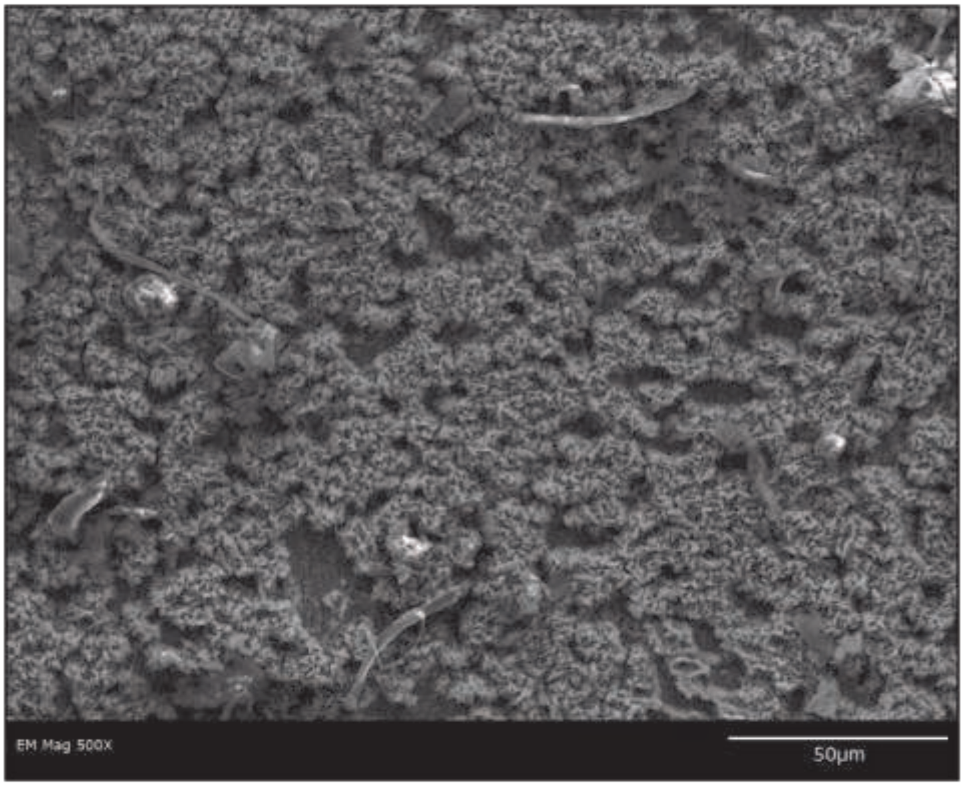

Figure 9.

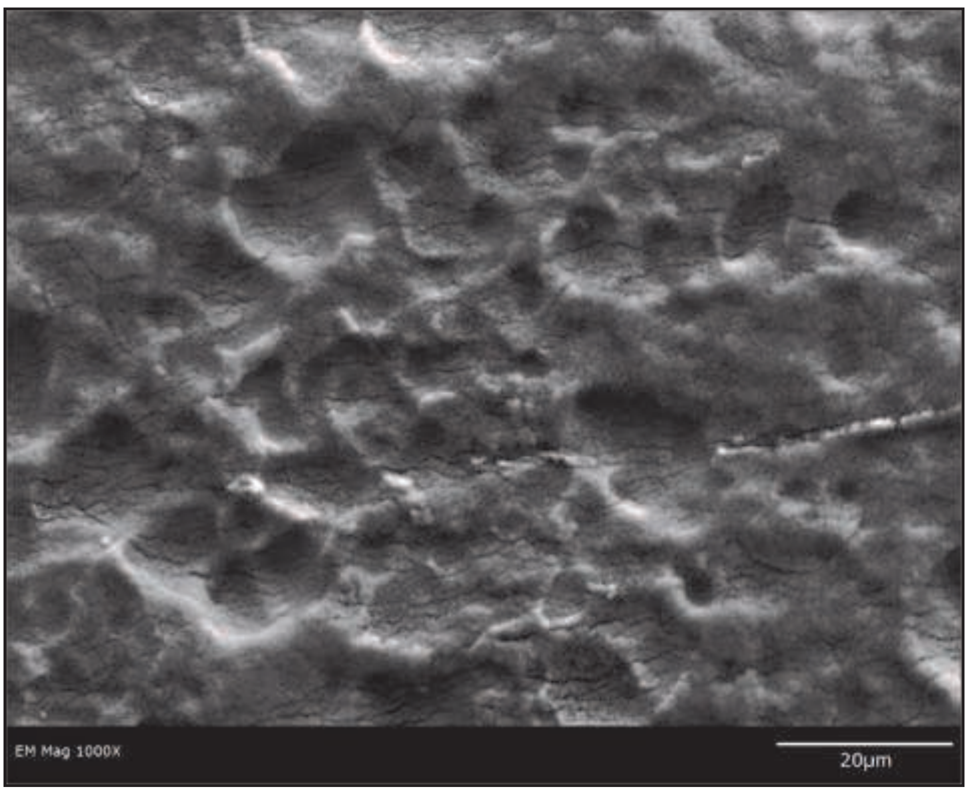

Figure 10.

water boxes on each end of both bars were relatively free of deposits. Some cracks were observed in the epoxy coating, but no spalling of the epoxy was observed (Figure 11).

Discussion

M&M Engineering identified several restricted and plugged strand locations in the two stator bars received for examination. No spalled epoxy was identified at these locations. The deposits resulting in restriction and plugging of the strands was due to the formation and accumulation of copper oxide CuO (tenorite). Tenorite forms in environments containing dissolved oxygen. The unit from which these sample bars were removed is operated with part per million levels of dissolved oxygen therefore the formation of tenorite could be expected in this system. However, typically once a copper oxide has formed, it acts as a protective layer and should remain in place. In the case of the generator strands, it appears that in some areas this layer spalls from the surface and collects to form a plug or forms a bridge across the strand until a plug is formed.

It is not clear why the thicker tenorite layer forms and why it releases in specific areas. That the released tenorite deposits collect predominantly in bends is consistent with industry experience and is likely flow related. Review of published literature found several articles discussing the formation of copper oxide (CuO)

(Continued from page 6)

whiskers[1, 2] and dendrites[3]. The formations described are similar to the needle-like structures observed in the strand deposits. However, the conditions under which the copper oxide (CuO) whiskers were formed included temperatures higher than would be expected in the stator bars (450°C). The dendritic structures described in the reference were formed in deionized water between copper electrodes. Neither of these conditions is experienced in the copper stator cooling strands. Therefore the driving force(s) behind the oxide growth and release cannot be explained at this time. Currently, it can be concluded that the epoxy did not contribute to the formation of the restrictions and plugs, neither did inappropriate water chemistry control as only copper was observed in the deposits. Additionally, the oxides in the plugs are formed under elevated dissolved oxygen conditions.

EPRI has studied conditions under which copper oxides are created in both low dissolved oxygen and high dissolved oxygen stator cooling water systems[4]. This research attempted to tie the release of copper oxide layers into the cooling water to specific conditions (including the electrochemical corrosion potential (ECP)) of the system. In both the stations documented by the EPRI report, where conditions were carefully monitored, the actual cause of the copper oxide release was not able to be tied to any specific event or chemistry. Subsequent testing has also been reported on a low-oxygen system and changes in ECP ahead of a copper oxide release event[5].

This research is unique in that it shows clearly that there are areas of corrosion on the inner surface of the stator bars that cause pitting to occur versus simply the formation and release of a passive

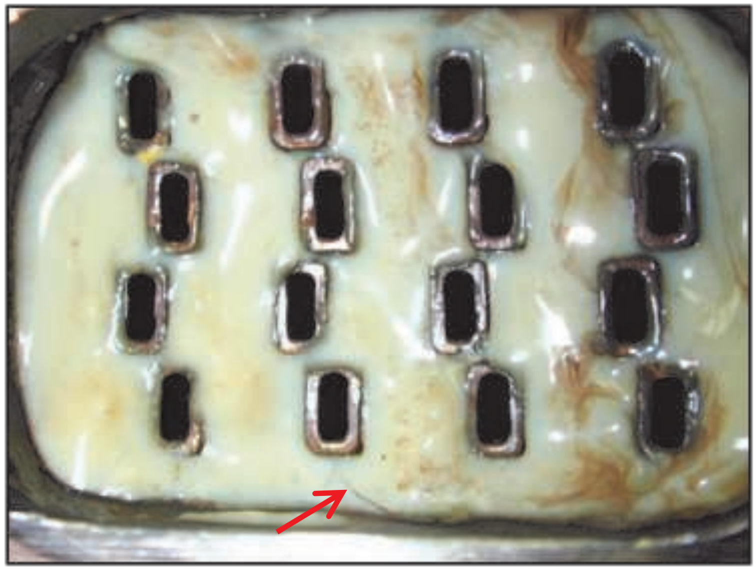

Figure 11.

tenorite layer, as has been the focus of previous work. The pitting in this high-dissolved oxygen system may have many potential sources. In three cases, EDS spectra found traces of chloride and in one case sulfur in the deposits, yet the continuous side-stream deionization should be continuously removing any soluble chloride or sulfate in the stator cooling water. Additional research would be needed to determine if these strands could have contained chloride and sulfate containing-deposits when the stator was new or if the water had been contaminated subsequently.

1 “Copious whisker growth on copper scale”; F. Morin; Journal of Materials Science Letters 2; 1983; pp 383 - 384.
2 Stress Driven Oxide Whisker Formation During the Thermal Oxidation of Metals”; L. Yuan and G. Zhou.
3 “Dendrite Formation by Copper Ion Migration in Printed Wiring Board”; H. Habaki, et al; Thammasat International Journal of Science Technology, Volume 13, Special Edition; November 2008; pp 6 – 10.
4 Electrochemical Corrosion Potential (ECP) of Hollow Copper Strands in Water Cooled Generators, 1014813 (Vol 1 and 2), March 2007, EPRI Palo Alto, CA
5 R. Svoboda.” Monitoring Stator Cooling Water Chemistry by the Electrochemical Potential” PPChem 2011, 13(8), 496-502

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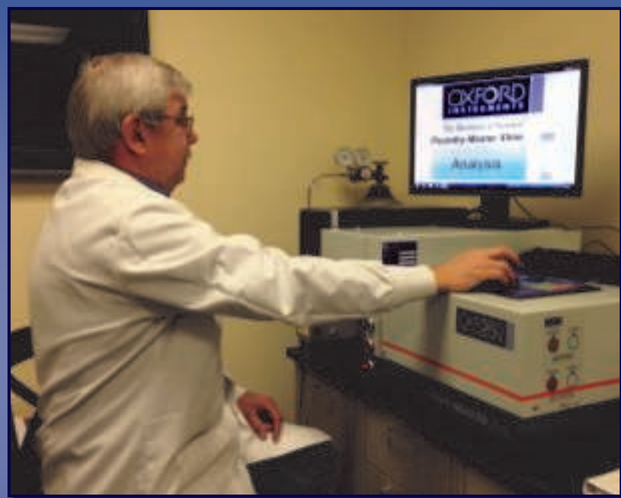
ANNOUNCEMENTS

It's here!

Oxford Instruments Foundry-Master Xline Spectrometer (OES)



M&M Engineering is pleased to announce the arrival of our newly purchased Oxford Instruments Foundry-Master Xline spectrometer (OES). We can now perform certified compositional analysis of carbon, low alloy and stainless steel materials in-house. This allows us to offer material identification in less than 24 hours, complementing our other metallurgical and analytical services, that includes metallographic sample preparation, hardness testing, microhardness testing, energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM).

Did you know…

On February 26, 2014 in the Federal Register, the Environmental Protection Agency (EPA) issued a NODA (Notice of Data Availability) in support of the proposed rule titled "Standards of Performance for Greenhouse Gas Emissions From New Stationary Sources: Electric Utility Generating Units" that was published on January 8, 2014. The EPA is soliciting comments on its interpretation on the provisions in the Energy Policy Act of 2005. The deadline for Comments has been extended and must be received on or before May 9th, 2014.

SUMMARY: The EPA is issuing this NODA in support of the proposed rule titled "Standards of Performance for Greenhouse Gas Emissions From New Stationary Sources: Electric Utility Generating Units" that was published on January 8, 2014. Through this NODA and the technical support document it references, the EPA solicits comment on its interpretation of the provisions in the Energy Policy Act of 2005, including the federal tax credits contained in that Act, which limit the EPA's authority to rely on information from facilities that received assistance under that Act. The EPA believes those provisions do not alter the EPA's determination in the proposed rule that the best system of emission reduction for new fossil fuel-fired boiler and integrated gasification combined cycle electric utility generating units is partial carbon capture and sequestration.

To see more details and to submit comments, visit: http://gcs.regscan.com/gcs/Pages/index.html?run=esrch.exe&uid=412834966309954&aid=1&db=REG0214&doc=180001ID.HTM&dte=2%2F26%2F14&query=&hc=0&ofs=

MIC in Stainless Steel Tubes

By: Catherine Noble
Senior Engineer

Three condenser tube samples manufactured from Type 304L stainless steel were received for examination because they contained multiple perforations. The tubes had only been in operation for one year and were from a condenser that had a vapor product containing formaldehyde, melamine, and other chemicals on the tube side and chilled cooling tower water on the shell side. Other condensers within the same facility were running with the same tube material (but with older installations) and the same cooling water, but had not had leakage problems. M&M Engineering was asked to perform an analysis of the condenser tube samples in an effort to determine the cause of leakage in the almost new stainless steel tubes.

The perforations appeared to initiate from the external surface (cooling water side) and had rust-colored rings surrounding each leak (Figure 1). The rust colored rings were suggestive of tubercles or bacteria slime colonies surrounding the leaks characteristic of microbiologically influenced corrosion (MIC). In addition, all of the perforations were on the tops of the tubes as they were positioned horizontally in the condenser. After examining the external surfaces, all of the tube sections were longitudinally split to facilitate examination of the internal surfaces. Visual examination of the internal surfaces revealed corrosion and staining around the area of each perforation, no deposit build-up or corrosion was noted on the internal surface remote from the observed through wall perforations.

Two perforations were selected for further examination, and both were observed in more detail. The cross-sections showed that the pitting initiated on the external surfaces of the tubes usually at the longitudinal seam weld. Not all of the pitting on the three tube samples was adjacent to the welds since the perforations were not all in a straight line; however, the corrosion was preferential to the welds and the heat affected zone (HAZ) of the welds. The pitting was

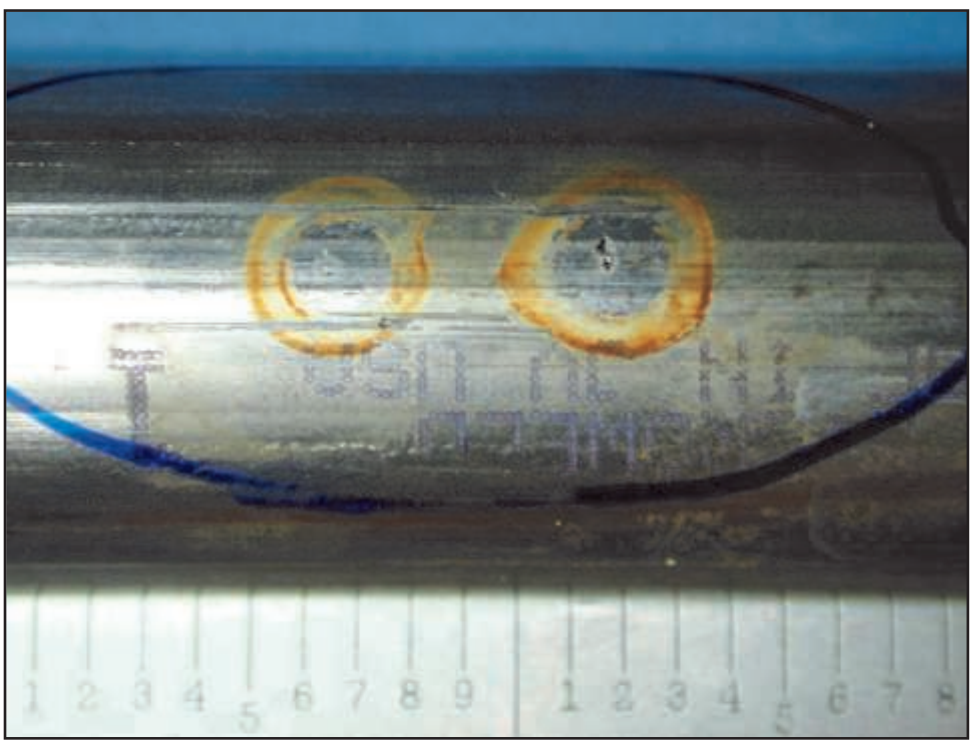


Figure 1.

undercut and progressed through the entire wall thickness (Figure 2 and 3). The undercut nature is indicative of MIC.

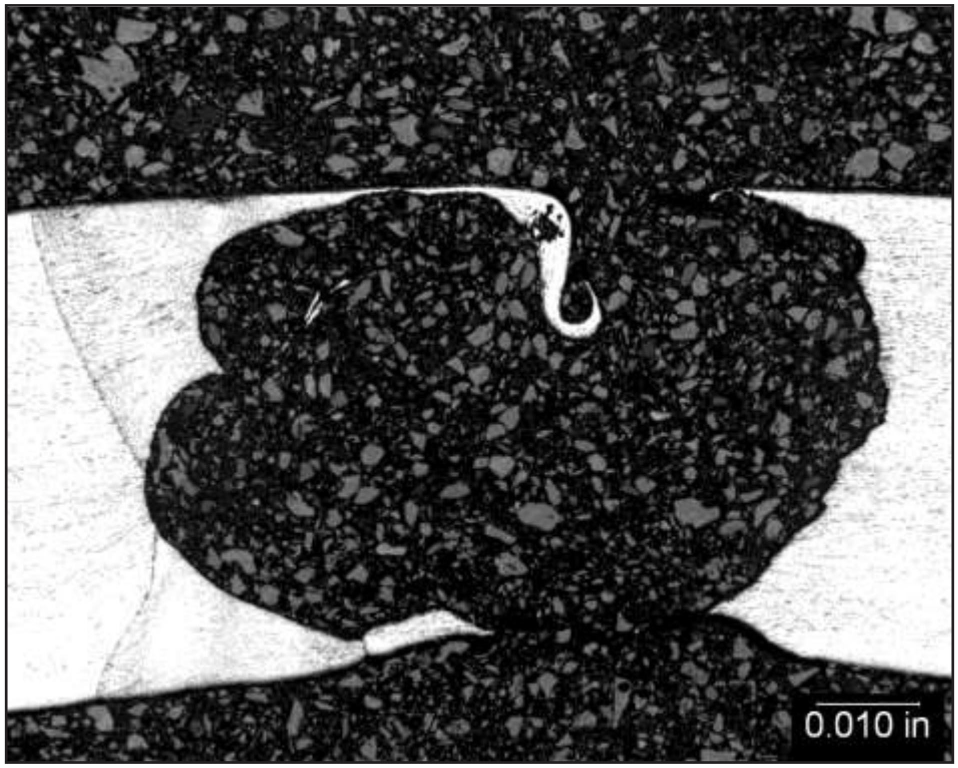


Figure 2.

The typical external and internal surface of the tube samples, remote from any noted pitting, was examined. The observed microstructure was considered typical for Type 304 stainless steel with no surface anomalies or metallurgical defects observed.

The rust-colored ring deposit surrounding one of the perforation on the external surface was analyzed *in situ* using energy dispersive X-ray spectroscopy (EDS[1]) in the scanning electron microscope (SEM) to determine its elemental composition (Figure 4). The ring deposit consisted primarily of oxygen, iron, silicon, chromium, and carbon. Smaller to trace amounts of calcium, sodium, aluminum, nickel, potassium, chlorine, phosphorus, sulfur, titanium, magnesium, and manganese were also detected. Chlorine and sulfur can be associated with various types of bacteria that can cause MIC. The carbon was also high, indicating that something organic such as bacteria could be present. None of the other elements were out of the ordinary for stainless steel tubes exposed to treated cooling water.

A portion of one of the tubes containing three perforations with external ring deposits was removed and analyzed using DNA testing methods to identify microbiological species present in the deposit. DNA testing can identify the type of bacterial DNA found in the sample sediment and assign a relative percentage of each bacterial genus identified from a library of bacterial genus-specific probes. DNA analysis confirmed the presence of "metal depositing" bacteria, "nitrifying" bacteria, and "slime producing" bacteria.

Iron-depositing bacterium (IDBs) was identified in the deposit, which is known to be the most aggressive form of bacterial species to stainless steel alloys. The specific strain detected was Gallionella. IDBs are capable of laying down deposits on metal surfaces and can oxidize ferrous ions to ferric ions. The deposition of cathodically reactive ferric oxides, and the consumption of oxygen by bacterial respiration within such deposits, can lead to a breakdown in the protective oxide film on the stainless steel and lead to pitting. The iron-depositing bacterium also has the ability to concentrate chlorides, which is aggressive to some stainless steel alloys.

Slime producing bacteria can also lead to localized MIC attack of stainless steels. Slime is primarily a

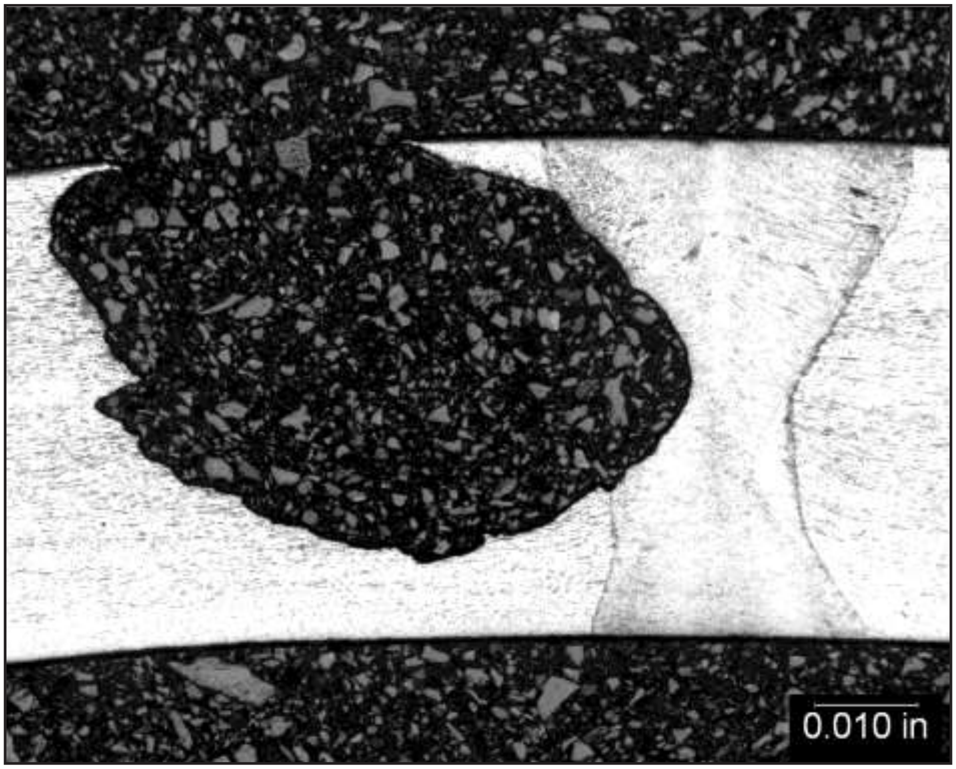


Figure 3.

problem because it can concentrate chlorides in an under-deposit manner leading to pitting or even environmental cracking; no cracking was observed in the analyzed tube section. Slime can live in conjunction with other MIC-producing bacteria, such as the identified IDBs. The bacteria identified in the tube sample were denitrifying bacteria that consume nitrates to produce ammonia. This is normally corrosive only to copper alloys, but the bacteria can still cause the problems described above. The presence of denitrifying bacteria should also be of concern where there are copper components.

Nitrifying bacteria convert ammonia or nitrite into nitrate and are not considered harmful to stainless steels.

The stainless steel condenser tubes contained multiple external surface-initiated perforations. Through-wall penetrations of stainless steel due to microbiologically influenced corrosion (MIC) may be caused by Gallionella (or similar iron oxidizing organisms) which typically result in rust color streaks emanating from the penetration, as seen on these samples. Dried-out deposit colonies in ring form were noted in the areas of localized pitting. The color of the deposits (reddish-brown) is also characteristic of MIC caused by iron oxidizers.

Metallographic examination at identified corrosion revealed that the corrosion initiated on the external surface. MIC of stainless steel is often very localized with a small penetration at the metal interface with more extensive corrosion under the surface or tunneling, as noted in the tube samples. There are many bacterial species that produce acids of sufficient concentration to breakdown the protective oxide layer on the stainless steel. Once breached, bacterial colonies continue to grow and generate pits beneath the metal surface. Chloride ion concentration under the biofilm layers accelerates the acidic attack of the metal. MIC corrosion tends to be very localized, occurring only under the established biofilm. This is different from chloride pitting attack, which tends to be more generalized across the metal surface. Pitting due to MIC is generally isolated and produces single pinhole failures.

Chemical analysis determined that the composition of the stainless steel matched Type S30403, or Type 304L stainless steel. No material deficiency or manufacturing defect contributed to the failure. However, Type 304L stainless steel is known to be a susceptible material to MIC and more pit-

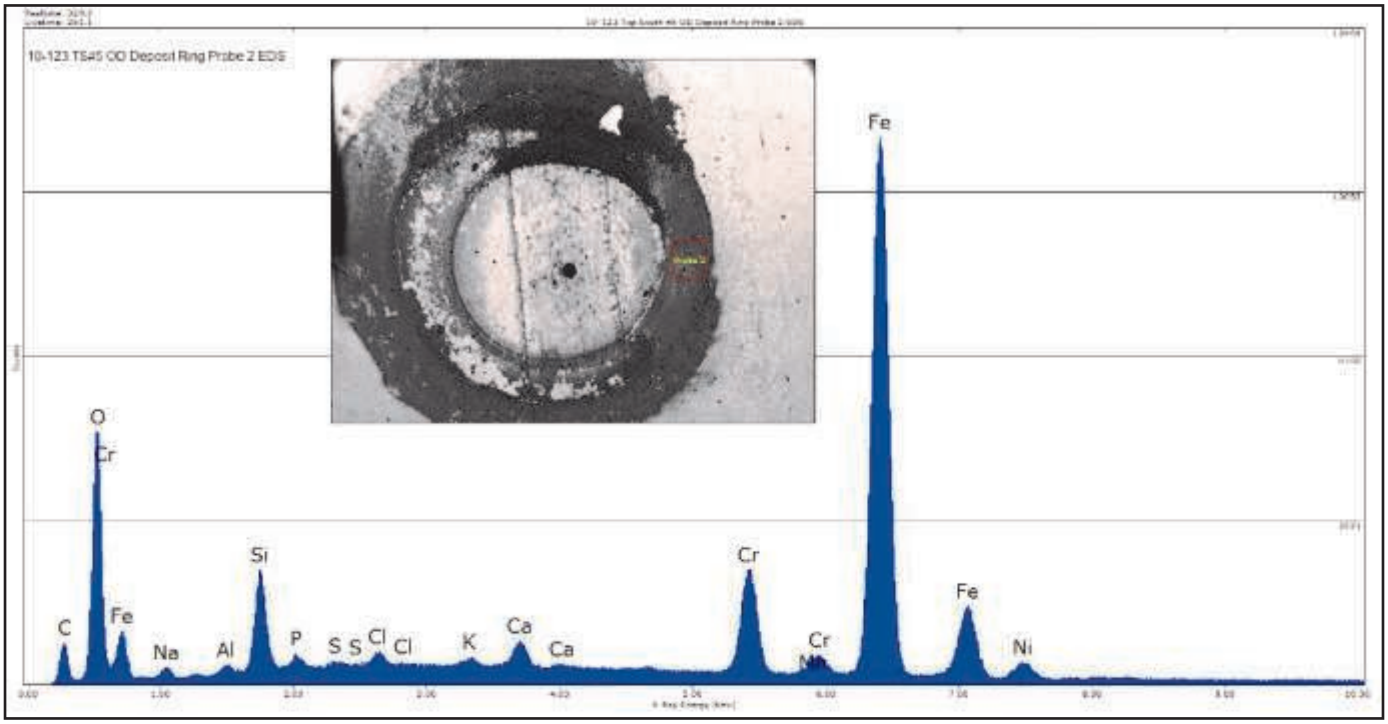


Figure 4.

resistant stainless steels have been specified and can be selected as replacement. The tube material should have a pitting resistance equivalent number (PREN) of at least 34. Alloys with PRENs greater than 34 include "super" stainless steels such as higher molybdenum austenitics, high chromium ferritic stainless steels, or duplex grades. Additional replacements could include nickel-based alloys or titanium. In addition, the welds in any new metallic piping system should be made in a way that minimizes their susceptibility to localized corrosion (i.e. smooth weld contours). The smoothness of the surface is also a factor. For example, an electro-polished surface will be more resistant to this attack than a standard mill finish simply because it is more difficult for bacteria to gain a "foothold" on the smooth surface.

It is unclear why the older condensers using the same tube material and cooling water had not also experienced MIC issues, but one likely possibility is that the older tubes had a chance to fully passivate and form more cohesive protective oxide layers before the bacteria entered the system. Another potential scenario is that a large percentage of the tubes were oriented with the seam welds on the 12 o'clock position compared to the previous installations. With corrosion preferential to the welds, having the susceptible area in a favorable orientation would increase the likelihood of corrosion.

[1]EDS provides qualitative elemental analysis of materials under scanning electron microscope (SEM) examination, based on characteristic energies of X-rays produced by the electron beam striking the sample. With a light element detector, EDS can detect the elements with atomic number 5 (boron) and above. Elements with atomic number 13 (aluminum) or higher can be detected at concentrations as low as 0.2 weight percent; lighter elements are detectable at somewhat higher concentrations. As performed in this examination, EDS cannot detect the elements less than atomic number 5 (i.e., beryllium, lithium, helium, or hydrogen). The results of this analysis are qualitative and indicate relative amounts of the elemental constituents. The EDS results were quantified using a standardless semi quantification (SQ) method. SQ electronically analyzes the EDS results, thereby lowering the detection limit to about 0.1 weight percent.

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M&M ENGINEERING ASSOCIATES, INC.

Preventing Failures in Steam Generating Equipment

This event Sold Out!

February 19-20, 2014
Austin, Texas

Thank you to all who attended and helped to make this year's workshop such a great success.
We are thrilled with the participation demonstrated during class sessions and at our Facility and Laboratory Open House.

M&M Engineering hosted its 3rd annual training class for producers of steam, be it used in power or process applications. The two day workshop focused on the issues most common in steam generating systems and is applicable to many industries including: pulp and paper, refining, petro-chemical, and power generation.

Day 1

- Equipment Associated with Steam Generation – A Primer
- Utility Feedwater Heaters and Damage Mechanisms
- Water Touched Boiler Tube Damage Mechanisms
- Steam Touched Boiler Tube Failure Mechanisms
- Introduction to Nondestructive Testing & Inspection Contracting
- High Energy Piping: Damage Mechanisms and Corrections
- Introduction to Failure Analysis

Day 2

- Failure Investigation Principles for Combustion Turbines
- Basic Turbine Failures
- Condenser and Cooling Water Failures
- Damage Mechanisms in Deaerators
- Water and Steam Chemistry-Influenced Failures in the Steam Cycle
- Discussion and Wrap Up

ENCORE! A Fall Session

Due to an overwhelming interest in our February workshop, M&M Engineering is considering a Fall Session. A final date will be decided based on the number of pre-registered attendees by July 1st, 2014.

If you would like to be added to the pre-registration list for the Fall Session, please let us know by emailing Lalena_Kelly@mmegineering.com or call (512) 407-3775 to be added to our tentative roster.

Seminars & Workshops

Catherine Noble, Senior Engineer with M&M Engineering attended the HRSG User's Group 22nd Annual Conference and Exposition, February 24-26, 2014.

22nd Annual Conference & Exposition

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CORROSION 2014

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Symposia

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March 9-13, 2014 • Henry B. Gonzalez Convention Center • San Antonio, Texas

Catherine Noble, Senior Engineer with M&M Engineering presented her technical paper entitled "SCC in Paper Mills – Unexpected Locations for an Expected Corrosion Mechanism" on March 12th. This symposium contains technical papers on corrosion control in the pulping, papermaking, and biomass conversion industries. Corrosion Control in Pulping, Papermaking, and Biomass Conversion Industries Sponsored by STG 38. Chair: Michael Lykins, Vice Chair: Catherine Noble.

On March 12th, 2014, Oscar Quintero, Metallurgical and Materials Engineer with M&M Engineering presented "Failure Analysis of a Superheater Tube". Industries: Water and Wastewater, Chemical Inhibitors, Materials Selection and Design, Energy Generation, Transmission and Distribution.

David Daniels, Senior Principal Scientist with M&M Engineering will be presenting:

HRSG and High Pressure Boiler Water Treatment Operation

This workshop will cover the water quality required for high pressure (>900 psig/60 bar) steam boilers including the various treatments being used and new developments relative to protection from scale and corrosion. The course will also cover treatment issues related to pre-boiler systems and the condensate systems and a discussion of controls and troubleshooting techniques. Operators, utility plant supervisors, managers, and engineers can all benefit greatly from the practical information provided in this course.

75 YEARS 1939-2014

INTERNATIONAL WATER CONFERENCE

NOVEMBER 16- 20, 2014

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Early Registration for the International Water Conference will be opening soon.

the Conduit is distributed free of charge by M&M Engineering Associates, Inc. We welcome your comments, questions, and suggestions, and we encourage you to submit articles for publication.

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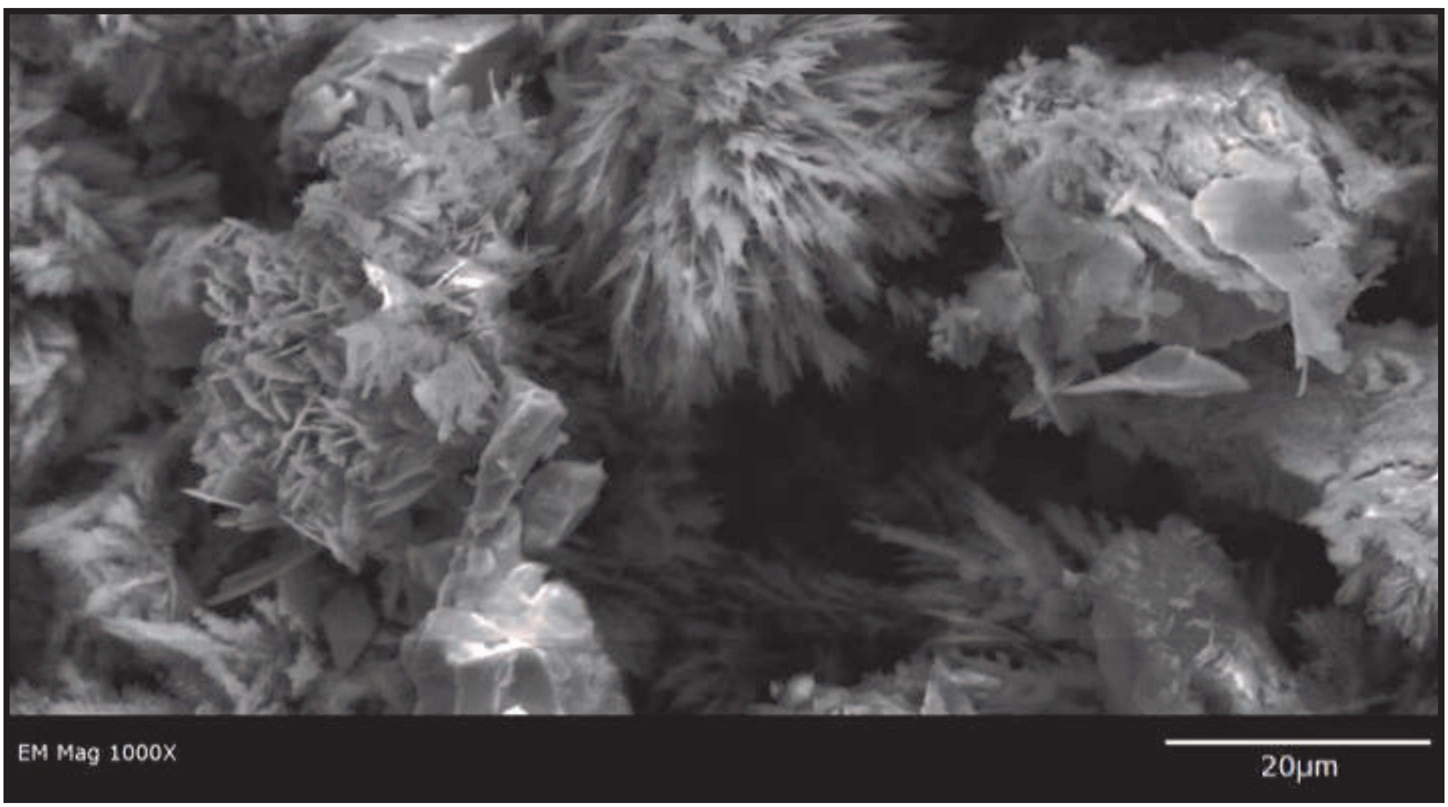
The Metal Never Lies



"Tenorite Bouquets in Bloom" (1000X)