



# the Conduit



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## Glossary of Boiler Tube Microstructures and Its Use to Verify Oxide Thickness Temperature Estimations

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The following is a summary of an article written for CORROSION 2011, but with new case studies. The full article can be obtained at [www.nace.org](http://www.nace.org) → Store → Conference Papers.

### INTRODUCTION

It is difficult to know what exact temperature a boiler tube has been exposed to over its lifetime. When this information is needed for a tube analysis, one possibility is to calculate an equivalent tube metal temperature

using the oxide scale thickness and published data. However, this method is not extremely reliable because of the multiple factors that can affect / disturb oxide growth.

M&M Engineering Associates, Inc. has an ongoing research project that examines microstructures of common boiler materials as they are affected by varying thermal exposures. With these "standard" microstructures available to compare with incoming failures, one can increase the confidence level of the temperature exposure of the tube. The data can also be used to confirm a tube's temperature exposure that was

determined using the oxide thickness method.

### PROCEDURE

An aging schedule was established to examine the materials at various levels of heat exposure for assorted lengths of time. The materials were exposed to lower temperatures for longer times and higher temperatures for shorter times to more realistically reflect actual life operations. Carbon steels were aged at temperatures ranging from 900°F to 1600°F with exposure times ranging from 1000 hours for lower temperatures to 1

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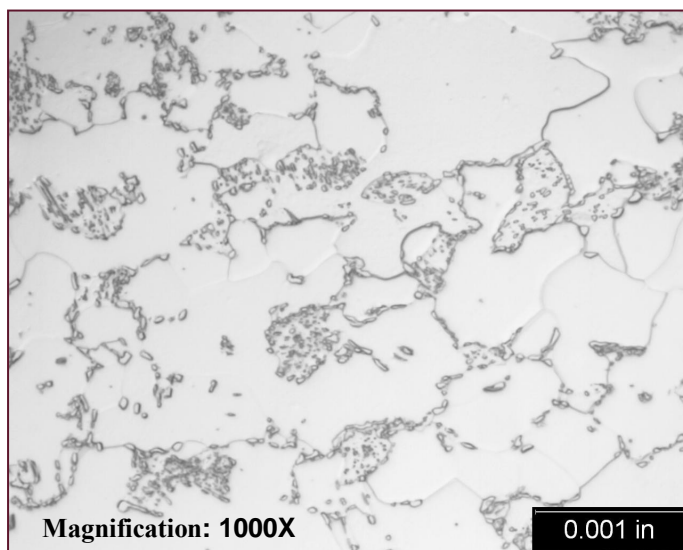
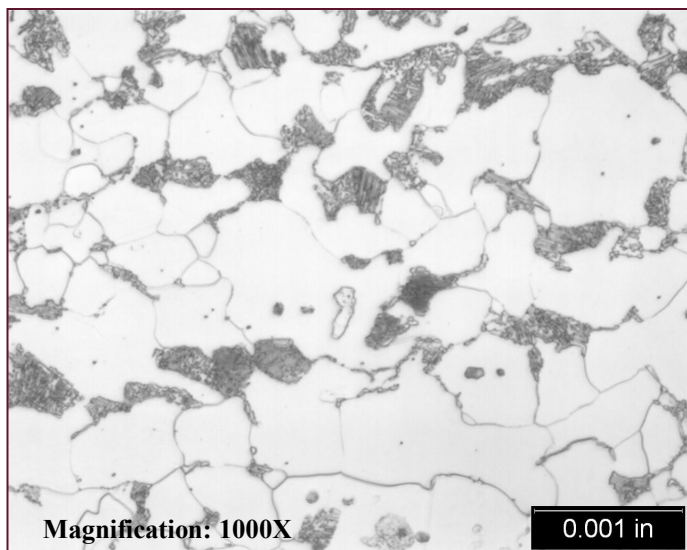


Figure 1: Photomicrographs show SA-210, Grade A-1 in the as-received condition and after 5 hours at 1300°F (704°C). 0.010 inch is equivalent to 0.254 mm. Sample was etched using Picral-Nital.

(Continued from page 1)

hour for higher temperatures. Alloy steels were aged at temperatures ranging from 1125°F to 1650°F with exposure times ranging from 1500 hours for lower temperatures to 1 hour for higher temperatures. Materials were also examined in the as-received condition. Materials that have already been examined in the heat treatment study include alloy grades from the following ASTM specifications: A178, A192, A210, A285, A515, and A213. After heat treatment, each sample was prepared for metallography and documented at various magnifications. Hardness was also measured.

### HISTORY

One of the earliest uses of this glossary was to quantify the extent and duration of overheating of a coal gasifier. The vessel had been in service approximately ten years with tube metal operating temperatures of approximately 950°F. The vessel was subjected to a hostile fire that visibly overheated and distorted portions of the vessel. The damage was thought to be localized to one repairable region, but the vessel owner wanted to be certain that all damage was repaired. Conversely, his insurance company did not want to pay to replace "good tubing." Metallographic sections were removed from specific areas of the vessel and a temperature profile established. The tube exposure temperatures were estimated from the tubing microstructures and a reasonable repair plan was formulated. The vessel owner and their insurance carrier were pleased with the outcome.

### EXAMPLE

As an example of the use of the glossary, SA-210, Grade A-1 is

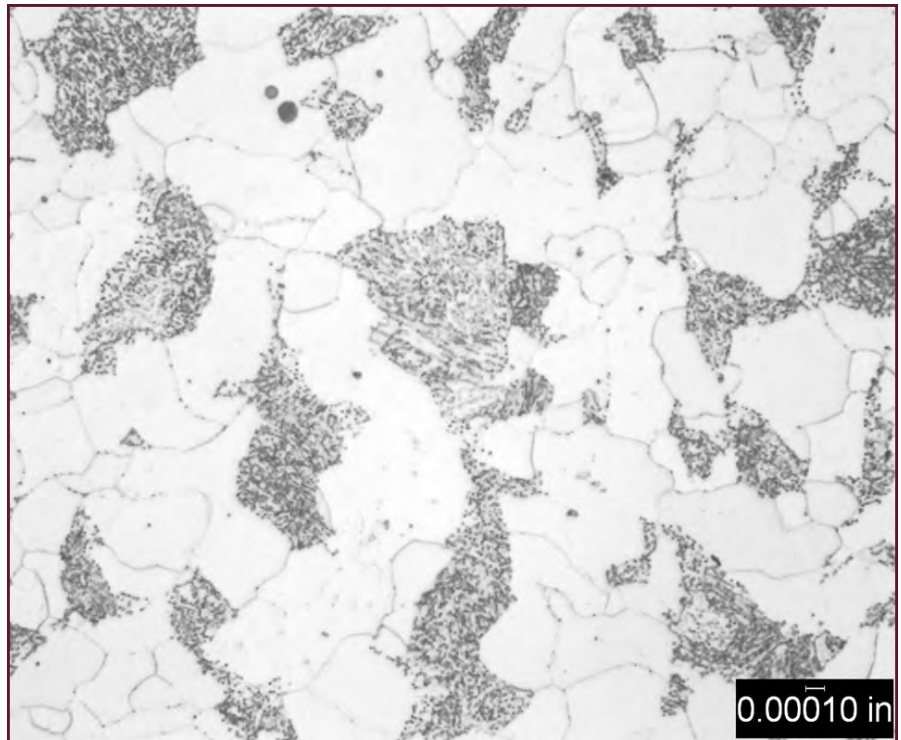


Figure 2. Photomicrograph shows the condition of the T2 superheater tube after 60,000 hours of service. Sample was etched using Picral-Nital.

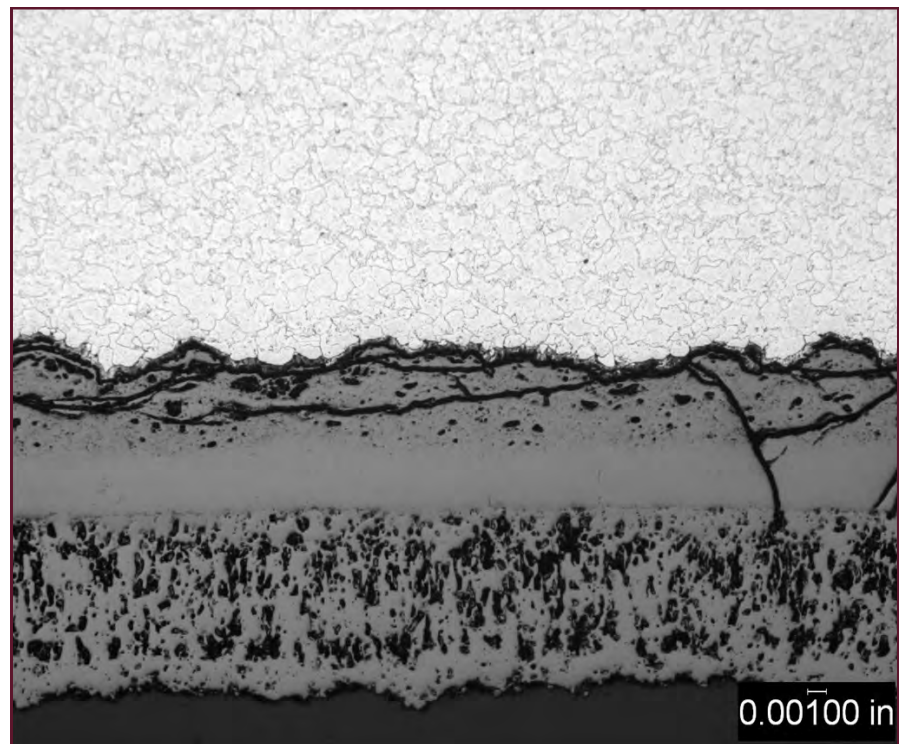


Figure 3. Photomicrograph shows the oxide thickness (0.020 inch) on the internal surface of a T2 superheater tube. Sample was etched using Picral-Nital .

compared as-received and after heat exposure to show the change in microstructure. SA-210, Grade A-I is a medium-carbon steel commonly used in boiler and superheater tubes and has a maximum of 0.27 percent carbon. The as-received microstructure of the A-I material (shown in Figure 1) is a mixture of ferrite and pearlite. This can be compared to the microstructure after five hours at 1300°F (704°C), also shown in Figure 1. As the material ages, the carbide morphology in the pearlite breaks down. Initially, the small discrete carbides on the crystallographic planes agglomerate into larger, more visible precipitates. With additional time, these carbides further degrade and release carbon that migrates to the grain boundaries and forms an intergranular carbide precipitate.

### CASE STUDY

A superheater tube was received for a metallurgical assessment. The tube was made of SA-213, Grade T2<sup>2</sup> and had been in service for approximately 60,000 hours. No failure was observed in this tube sample; however, several failures occurred in this particular superheater. The microstructure of the tube is shown in Figure 2 and was typical of like-new T2 material with bainite colonies and dispersed carbides. The internal oxide thickness was measured as 0.020 inch (0.051 cm), which is unreasonably large for a tube with so few operating hours (Figure 3). Using internal oxidation growth rate data available for chromium-molybdenum steels<sup>3, 4</sup>, this translates to an equivalent tube temperature between 1200°F (649°C) and 1300°F (704°C). However, the microstructure in Figure 2 is not consistent with this calculated temperature exposure and is more in-

line with the as-received condition of T2. The microstructure shows that the oxide thickness measurement was not a good estimate of operating temperature and the oxide was the result of some other process. In this case, some of the deposit likely resulted from carry-over from the steam circuit and was not formed *in situ*.

### CONCLUSIONS

Developing a glossary of microstructures is a useful tool in determining the temperature exposure that an alloy has experienced. Having a standard reference condition makes it possible to confirm operational data concerning temperature profiles and also provides a check for using oxide thickness measurements to estimate equivalent operating temperatures. Additional alloys are being added to this study, and service-aged samples are also being added to the database.

### REFERENCES

1. ASTM<sup>(1)</sup> A 210 (2010), "Standard Specification for Seamless Medium-Welded Carbon Steel and Carbon-Manganese Steel Boiler and Superheater Tubes" (West Conshohocken, PA: ASTM).
  2. ASTM A 213 (2010), "Standard Specification for Seamless Ferritic and Austenitic Alloy-Steel Boiler, Superheater, and Heat-Exchanger Tubes" (West Conshohocken, PA: ASTM).
  3. R. Viswanathan, *Damage Mechanisms and Life Assessment of High-Temperature Components* (Metals Park, OH: ASM International, 1989), p. 229.
  4. S.R. Paterson, T.W. Rettig, "Remaining Life Estimation of Boiler Pressure Parts-2 1/4 Cr-1Mo Superheater and Reheater Tubes," Project RP 2253-5, Final Report (Palo Alto, CA: Electric Power Research Institute, 1987).
- (1) ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

## Dealloying/Selective Leaching of Copper Alloys due to Microbiologically Influenced Corrosion (MIC) in Heat Exchangers

**By Spencer Rex  
Mechanical Engineer  
and  
David Daniels  
Principal Scientist**

Copper alloys have been used extensively in a number of industrial water cooled heat exchangers because of their excellent thermal conductivity properties. A disadvantage of these materials is that they are relatively soft and will corrode for a variety of reasons. Copper alloys that have been used in industrial heat exchanger applications include, 66.5Ni/31.5Cu/Fe (Alloy 400 or N04400), 90Cu/10Ni (C70600), 70Cu/30Ni (C71500), and arsenical Admiralty Brass (44300).

Dealloying can occur in copper alloy heat exchanger tubing caused by microbiologically induced corrosion (MIC), particularly in Admiralty Brass. Bacteria, fungi, and algae all can be found in cooling water. Cooling towers act as large air filters, pulling in outside air that contains dust and bacterial spores into the tower where they are mixed with the cooling water. Many heat exchangers provide consistent warm temperatures and a continuous supply of aerated water--an excellent place for all types of microbiological species to take hold. When microbes settle on a surface they set up a protective organic layer called a biofilm, underneath which the microbes live protected from

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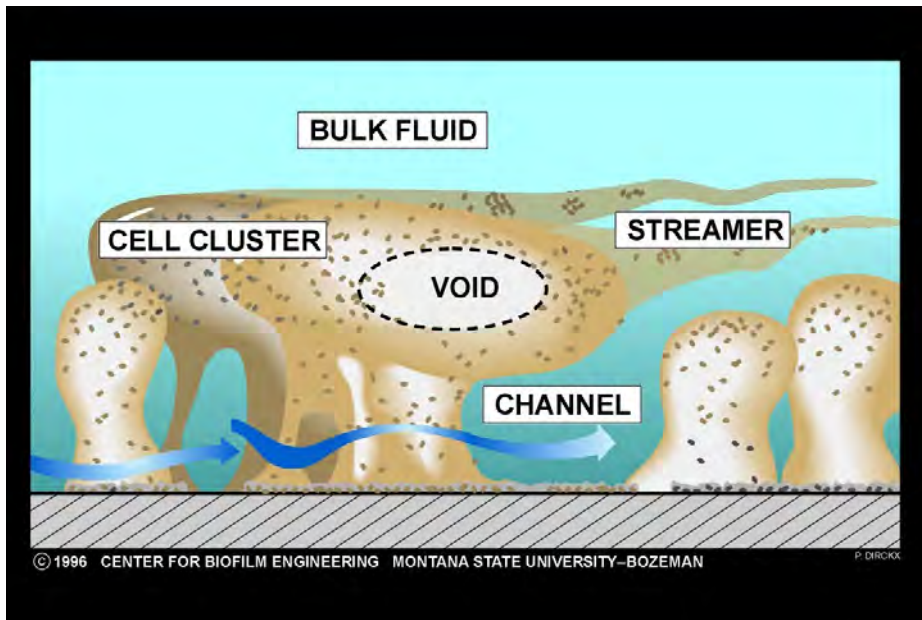


Figure 1. Biofilm

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environmental changes including biocide addition (Figure 1). Underneath the biofilm and adjacent to the metal surface, waste products from the bacterial respiration can accumulate. They are typically more acidic than the bulk cooling water. These conditions are conducive to dealloying of copper alloys. Dealloying will occur underneath the biofilm when all the components of the electrochemical/galvanic cell (cathode, anode and electrolyte) are in electrical contact with one another. In the case of dealloying of copper alloys, the copper acts as the cathode, the zinc or nickel or any other less

noble element in the alloy as the anode, and the water in the biofilm is the electrolyte.

The result of dealloying is a metal matrix where the less noble element in the alloy has oxidized, causing it to become soluble and dissolve. The remaining copper metal has a spongy appearance and the metal has changed from brass color to copper color (Figure 2). The copper sponge has very little remaining structural strength. This can lead to a brittle and sometimes catastrophic failure of the tube. The extent of the dealloying in this condenser tube can be seen in Figure 3. Figure 4 shows an elemental

dot map of the dealloyed area generated by energy dispersive X-ray spectroscopy (EDS). The dot map highlights the presence of a single element in the matrix, in this case nickel. Note the relative absence of nickel in the area where dealloying has taken place. Established biofilms are thicker and better at developing types of bacteria that generate strong corrosive acids. While there is nothing that can completely prevent biofilm formation, controlling biofilm development with biocides minimizes the potential for dealloying. In many cases, copper alloys are being replaced by stainless steel or titanium in condensers which are more corrosion resistant but have a lower thermal conductivity than copper alloys, so there is a trade-off. Also, stainless steel tubes are also susceptible to MIC attack.

To protect against dealloying of copper alloys by microbiologically influenced corrosion, the proper selection and concentration of biocides must be used control biofilms. Because biocides do not completely remove the biofilm, periodic mechanical removal of the biofilm (e.g., nylon bristle brushes or scrapers) and any debris in the tube, is critical.



Figure 2. Pure copper remains after the nickel has been removed.

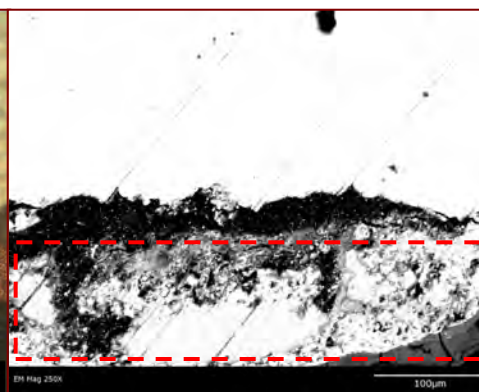


Figure 3. The area where dealloying has taken place is inside the red box. This same area is shown in Figure 4.

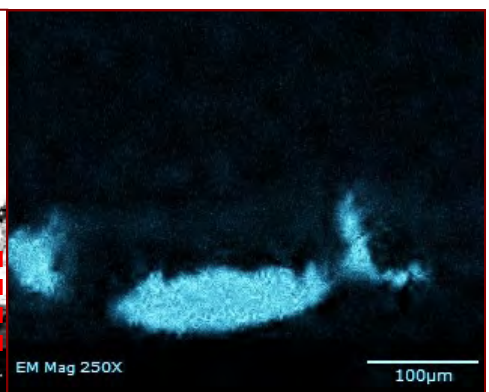


Figure 4. Absence of of Nickel (Blue) as seen in the EDS dotmap where the dealloying has occurred.

## M&M Engineering— Helping to Keep the Lights On and Life Sweet in Central Africa

**By David Daniels  
Principal Scientist**

A few years ago a sugar mill in Central Africa decided to upgrade a number of smaller bagasse boilers with a larger higher pressure (45 bar) boiler capable of not only generating the required mill steam but also a reliable source of electricity for the mill and the surrounding area. Up to that point, electrical power in the area had been sporadic. Power outages were common for one or two hours nearly every evening.

The mill purchased a 10 MW steam turbine with extraction points to supply the mill process and a small condenser for the remaining steam. After a short period of operation, the steam turbine developed performance issues. When the mill opened the steam turbine, they found it covered in white and rust colored deposits. Analysis showed that the deposits were predominantly silica and caustic. The turbine manufacturer recommended M&M Engineering to the mill. We visited the site, evaluated the water and steam chemistry program, determined the probable causes of the deposits and developed a plan for minimizing steam contamination in the future. The recommendations included changes in the boiler operation, chemical treatment, monitoring, and water pretreatment practices. We provided a new set of chemistry guidelines and provided training to the operators and lab personnel on testing, water treatment equipment, and handling

chemical upsets. The mill took action and made many of the recommended changes before the next campaign. A year later, M&M Engineering was asked to return during the mill outage where they were again removing the turbine cover for inspection. We found the turbine was far cleaner with minimal deposits. While there, we were able to find other ways for the plant to improve the reliability and reduce the costs associated with their steam cycle.

Sugar mills are net water producers as water from the cane is removed by a series of evaporators that concentrate the syrup to the point that it crystallizes. The various streams of condensed vapor from the evaporators are known as clean and dirty condensate depending on the propensity for the condensate to be contaminated not only with sugar, but also organic acids and alcohols that are part of the natural fermentation process. M&M Engineering worked with the mill to find appropriate ways to reuse water sources that otherwise were going to waste. The mill had a water pretreatment system that could be used to collect a relatively clean source of condensate known as VI for preparing boiler feedwater. This

resulted in far longer runs on the ion exchange demineralizer than they had experienced previously using a very hard well water. We also worked with the mill to revised the cooling tower chemistry program to allow them to use a source of “dirty condensate” as partial makeup to their cooling tower. This also reduced the mill’s use of a very highly mineralized well water for cooling tower makeup. This allows the cooling tower to operate at higher cycles of

**BEFORE**



**Figure 1. After only a short period of operation, the turbine became contaminated with deposits.**

**AFTER**



**Figure 2. The mill improved operating practices and chemical monitoring that made a tremendous improvement in the turbine’s appearance.**

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concentration with better control of scaling.

M&M Engineering continues to make annual visits to the mill to check on the boiler and steam chemistry, water pretreatment, and cooling water chemistry.

Now that the steam turbine issues have been resolved, the lights at the mill and in the surrounding area stay on constantly. Reducing the amount of well water used helps the mill and people in the area.

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### New Employees Join M&M Engineering



Anna Gentry joined M&M Engineering Associates, Inc. in May 2011 as a Mechanical Engineer. She has always been

interested in the way things work and taking them apart to find out just how. Anna holds a Master of Science in Mechanical Engineering from Texas Tech University with an emphasis in Mechanics and Materials. In graduate school she also explored the microscopic world while studying electron microscopy. Prior to joining M&M Engineering, Anna worked as a Stress Analysis Engineer helping to design, model, test and redesign the piping of a Naptha Hydrotreater Unit for an all new refinery to be built in South America. She also has experience in boots and a hardhat as a Field Engineer constructing full containment LNG tanks on the Gulf Coast of Texas. When not at work Anna likes to solve puzzles of the mathematical and jigsaw varieties, dance the Lindy Hop, enjoy the Texas Hill Country and crochet.



Candice Chastain joined M&M Engineering Associates, Inc. in February 2011 as an Administrative Assistant. Candice provides an

administrative backbone for the engineers, scientists and staff of M&M Engineering. She ensures that every proposal, report and presentation that goes out under the M&M Engineering name has the proper quality and polish. She also manages incoming calls for her coworkers, performs electronic and hardcopy archiving, handles multiple incoming and outgoing mail and freight services, plans events and conferences, and keeps the office up to date and organized. Before joining M&M Engineering, Candice lived in Fort Worth, Texas, where she was a small business owner, executive administrative assistant and an office manager several times over. She holds an Associate of Science Degree from North Central Texas College. Since moving down from the Fort Worth area, Candice has enjoyed gardening, cooking, wine and exploring Austin with her doggies.

### Seminars & Workshops



Ron Munson attended the International Gas Turbine Institute Conference in Vancouver, Canada June 6-10, 2011.



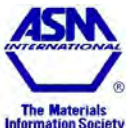
Jon McFarlen attended the ASME Power 2011 Conference in Denver, CO (July 12-14) and was a panelist for the "Aging of Combined Cycle Power Plants" discussion session.



TAPPI, the Technical Association of the Pulp and Paper Industry, had the PEERS conference in Portland, Oregon this year October 2- 5, 2011. Ron Lansing attended the TAPPI (Technical Association of the Pulp and Paper Industry ) Engineering Conference. M&M Engineering regularly participates in this conference and the Engineering Committees Corrosion and Materials sub-committee and task groups.



Jon McFarlen gave a presentation entitled *How to Assess the Health of High-Energy Piping Systems* on October 31, 2011 at the Combined Cycle Users Group 2011 meeting in San Antonio, Texas.



Henry Kight attended ASM International's training on *Metallography for Failure Analysis* in Cleveland, Ohio August 22-26, 2011

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All of us at M&M Engineering would like to take this opportunity to say thank you for contributing to our success and growth this past year. We sincerely hope that the upcoming year is filled with much happiness and prosperity for you and your family.

Have a joyous holiday season.