ENGINEERING ASSOCIATES, INC.

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

the Conduit

Winter 2007-2008

In this Issue

Stress Corrosion Cracking in an Ethanol Plant

By David Daniels

Fuel ethanol production is big business with ethanol plants springing up throughout the mid-West. In 2006, the United States produced over 4 billion gallons of ethanol fuel and national production goals have us producing 7.5 billion gallons by 2012. Our neighbors to the north are also joining the party. In December 2007, Canada announced a $1.5 billion biofuels program that will expand Canada's ethanol production to feed its biofuel requirements of 800 million gallons per year.

Ethanol plants are constructed of a combination of many different metallurgies with a preponderance of various grades of stainless steel. As such, they are susceptible to the multitude of problems that can plague these "corrosion-resistant" alloys. Since many of these plants use the same technology (they are often built by the same design firms), a problem at one plant will likely be

Figure 1. Multiple cracks on this stainless steel feedwater pre-heater tube actually started on the OD of the tube.

Mechanical & Materials (M&M) Engineering LLC is now M&M Engineering Associates, Inc. We are pleased to announce that the employees of M&M Engineering have purchased the business from its parent company, HSB Global Standards. We are the same staff, at the same locations, with the same telephone numbers and email addresses, providing the same services, just under new ownership.

M&M Engineering enjoyed 30 years of ownership by The Hartford Steam Boiler (HSB) Inspection and Insurance Company family of companies, beginning in 1977 as a part of Radian Corporation, and most recently as part of HSB Global Standards. However, with AIG's acquisition of HSB and AIG/HSB business expansion, M&M Engineering found itself more frequently in conflict of interest situations because of ownership by AIG/HSB. This affected our ability to provide services to our parent company as well as our commercial clients. Therefore, the time was right to become an independent company. Removing this conflict of interest barrier will allow us to better serve our clients, old and new, as a true third party independent consulting company. We are excited about the opportunities this brings to us and we are looking forward with great anticipation.

duplicated many times over.

Recently, M&M Engineering Associates, Inc. examined six finned stainless steel preheater tubes from an ethanol plant. The tubes contained numerous circumferential cracks that went all the way through the tube walls. However, there was very little deposit and no evidence of pitting or corrosion on the waterside surfaces (Figure 1).

The failed tubes came from the coolest section of a three-section economizer that takes heat from the gas of a thermal oxidizer after it passes through a heat recovery steam generator (HRSG) and just before it exits out the stack. The hottest section of this tubing is called the feedwater economizer and heats feedwater going to the HRSG. The middle section of tubing is called the cook water economizer as it heats water that cooks the corn slurry. These tubes are Type 304 stainless steel and the design gas temperature of the flue gas at the cook water economizer is about 300°F.

The last section of tubing is the feedwater preheater that heats makeup water prior to its going to the deaerator. Design temperature on the gas side of these tubes is about 250°F. On the waterside of the feedwater preheater, the temperature in the tubes is typically between 130°F and 185°F. The tubes are specified to be Type 304 stainless steel with fins of Type 409 stainless steel.

Figure 3. Deposits on the cook water tubes.

M&M Engineering found that the tubes in the feedwater preheater tubing failed due to chloride-induced stress corrosion cracking from the OD or gas side of the tube. The polished metallurgical samples found the classic branched cracking associated with this failure mechanism. (Figure 2) For stress corrosion cracking to form on the outside of the tube, chloride-containing water had to be sprayed onto the tubes and concentrated as the tubes were subjected to a number of wet-dry cycles.

Initially, it was suspected that there was a leak in the cook water tubing that contaminated the downstream tubes, but visual inspection of these tubes found no obvious leaks. However, there were deposits on the cook water tubes (Figure 3) and metallurgical analysis found incipient chloride stress corrosion cracking on these tubes also.

M&M Engineering was able to trace the source of the chloride and made recommendations to the plant to eliminate this as a potential source in the future.

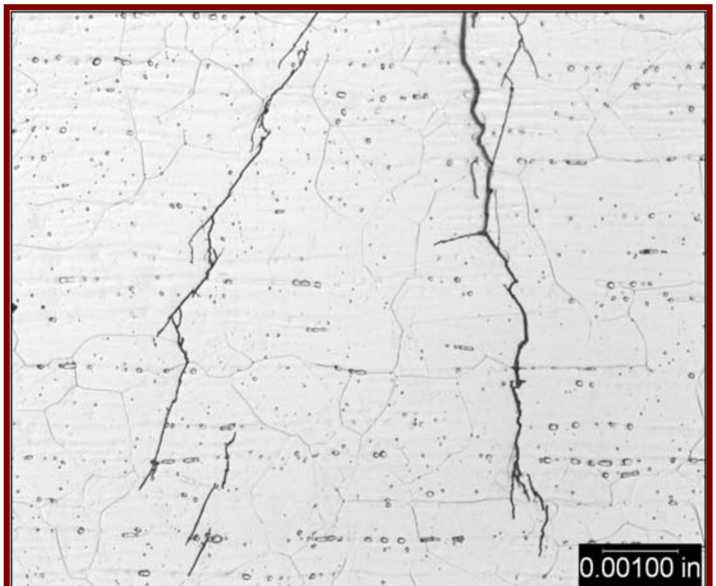

Figure 2. Classic branched cracking associated with this failure mechanism.

Corrosion in Once-Through Steam Generators Used for Oil Recovery (SAGD)

By Gary Loretitsch

Heavy (bitumen) oil from tar sands is produced using either conventional steam flood or the SAGD (steam assisted gravity drainage) method of recovery. In both cases the steam for injection is generated in once-through steam generators (OTSG) from blends of treated fresh water, treated brackish water, treated produced water, and reclaimed wastewater sources, including waste pond supernatant (overflow). The brackish water is pumped from deep water wells and the fresh water comes from conventional artesian wells. The water treatment trains for these water sources can include, oil/water separation, chlorination and de-chlorination, filtration, chemical (warm lime/MgO) softening with silica reduction (WLS), ion exchange (SAC and WAC), pH adjustment with liquid caustic soda, chemical de-oxygenation with sodium bisulfite, passivation enhancement with reducing agents, and further chemical treatment for boiler corrosion and deposit control.

Injection of steam-water fluids at these sites can range from 80% (or more) steam for common steam flood recovery to up to 100% steam for SAGD operations. The fields that require 80% to 100% steam for injection use steam separators in order to produce the superior quality steam needed to meet environmental regulations. These fields can either employ conventional treatment processes, as described above with polishing ion exchangers, or they can choose the alternative, multiple effect evaporation, which eliminates the need for other feedwater treatment processes.

Boiler feedwater treatment trains, from the deep wells themselves through the treatment process equipment, the feedwater booster pumps, the high and low pressure feedwater distribution lines have had and continue to have corrosion issues. Reliance on chemical de-oxygenation in lieu of thermal-mechanical deaeration has, in some cases, permitted corrosion of feedwater system components and boilers, which has been largely ascribed to *oxygen* pitting. Oxygen is a major cause but not the exclusive one for pitting damage. Consistent oxygen scavenging with sulfite ion and pH adjustment with caustic soda can serve to adequately protect carbon steel from oxygen pitting. However, there are other corrosion mechanisms capable of causing severe localized or pitting corrosion morphologies in boilers that are easily confused with oxygen pitting.

Some incidences of OTSG corrosion (Figure 1) are related to the recent increase in the bicarbonate alkalinity of the feedwater blend. Since the rate of replacement of fresh water and produced water with brackish well water is expected only to increase, it is essential to confirm the relationship between high alkalinity and boiler corrosion and to identify suitable corrosion control methods.

Boiler tubes provided to us clearly show two examples of severe localized corrosion, which are classic examples of FAC (flow assisted or accelerated corrosion). In one case, the dimpled or round-bottom pits, the longitudinal grooves in deep radial channels caused the loss of that magnetite film from erosion due to turbulent water flow within the temperature range required for FAC. In these boilers, magnetite formation/reformation is removed in part by the effect of carbonic acid formed when the carbon dioxide gas, liberated from the decomposition of bicarbonate alkalinity in the boiler water, re-dissolves in the water at the heat transfer surface of the tube. The repetition of this magnetite film formation and removal process is a corrosion mechanism and results in the extreme metal loss in the tube bend. Excessive alkalinity (and poor alkalinity and pH control) can also serve to accelerate dissolution of magnetite. This can be called a complex single-phase FAC .

Figure 1. OTSG return pass bend (longitudinal section) showing typical single-phase FAC "orange peel", along with grooves (merged pits).

Pinks and Blues

By Gary Loretitsch

Figure 1. Severely scaled floating head tube bundle (cooling water on shell side).

Routine analytical test procedures for field-use that are commonly used in water treatment are sometimes casually referred to as "Pinks and Blues." This vernacular somehow relegates the use of these procedures and the data that comes from them as passé at best and at worst, a waste of time. However, they are only less than important when the test results are misunderstood, misinterpreted or ignored. In addition, even professionals in the water treatment field can be guilty of overlooking the latent value in the "Pinks and Blues."

When sanitary wastewater is treated and reclaimed for reuse as cooling tower system make-up, one of the several significant dissolved solids in that water is phosphorus. Phosphorus is found in the phosphate radical referred to as phosphate and comes largely from synthetic detergents. Phosphate detergents are becoming less popular all the time, so the phosphate concentration in reclaimed wastewater has been trending down over the last twenty years or so.

Phosphate is sometimes removed incidentally if not purposefully when wastewater is clarified or partially softened using chemicals like lime and soda ash or caustic soda. Phosphate can be all but eliminated when iron salts are used as primary coagulant chemicals. Iron salts are preferred over aluminum coagulants in part because they can help a clarifier retain a higher percentage of the undissolved solids, called "floc", that would otherwise carry over and put a heavier than necessary load on the filtration system. Iron salts work very well for the reclamation plant, but if some of the iron should carry over in the reclaimed water plant's effluent, the users of the reclaimed water can find the iron troublesome, even damaging to their cooling systems. Refineries are probably the biggest users of reclaimed water and iron in the make-up to their cooling systems has the potential to cause them big problems. For this reason, refineries are wary of any changes in the way in which their reclaimed water supply is being treated.

Add to this the fact that a small amount of phosphate in reclaimed water is both a useful and a cost-effective corrosion inhibitor component of cooling water treatment programs in many refineries. So, while refineries are interested in limiting the iron content in their reclaimed water, they are also very interested in the phosphate in it. They want there to be enough phosphate in the water to provide protection from steel corrosion but not enough to cause heat exchanger fouling. Refineries and other plants using phosphate-based corrosion inhibitors usually add either polyphosphate or orthophosphate (or both) to supplement the phosphate indigenous to the reclaimed water. A select few of the test methods from the group called "Pinks and Blues" are used to analyze cooling water samples on a routine basis so that phosphates can be controlled within just the right concentration range. In fact, along with pH, calcium and conductivity testing, simple phosphate determinations are essential to maintaining control of all cooling water treatment programs, which depend in part on phosphate for carbon steel corrosion protection.

There are several variations of the basic "Molybdate Blue" orthophosphate test procedure. A few variations in the test procedure can allow a technician to differentiate between and compare concentrations of orthophosphate (simple molecules) and polyphosphate (condensed or complex phosphate molecules) and organic phosphate (phosphonate) in cooling water. To further complicate this picture, these procedures can be run using water samples that are either filtered or unfiltered before they are tested. Each test result contributes a piece of the "phosphate picture" in the cooling water. Just the right concentration ratio of orthophosphate to polyphosphate and phosphonate usually gives the best possible corrosion and fouling protection. For that reason, orthophosphate, polyphosphate, and phosphonate control tests are usually run routinely. That is, except when the routine of some of these particular phosphate "Pinks & Blues" is thought to be too time consuming or to produce unnecessary data. Whenever the consistent quality of the reclaim water (including its phosphate concentration) has been demonstrated, a comprehensive phosphate test regimen can seem like a good place to cut back to save time and trouble.

Presented here is an example of what can happen as a result of this kind of false economy. The orthophosphate in reclaimed water was supplemented by a refinery with a product containing polyphosphate. This product provided polyphosphate, some percentage of which hydrolyzed in the cooling water to orthophosphate as anticipated. Initially, the refinery tested cooling water samples for orthophosphate with one procedure and for polyphosphate with a slightly modified "Total Phosphate" procedure. The difference between the results of these two tests on the same water sample yielded the polyphosphate concentration specifically. The data from these two tests provided the information needed to adjust the dosage of the polyphosphate product that the refinery was feeding. After many months, however, it was noticed that the control test results were predictable. That is, the required injection rate of the polyphosphate product appeared to be directly proportional to the make-up (reclaimed water) rate. For that reason, it was decided to rely upon only the orthophosphate procedure for control of the phosphate product injection.

Sometime thereafter, the reclaimed water provider advised the refinery that a change in the chemistry of the reclamation process would result in reclaimed water with a much lower orthophosphate concentration. Since the refinery was already set up to inject supplementary polyphosphate product, it was thought that an increased dosage of this product would make up for the "missing" phosphate. And this is exactly what happened. The dosage of the polyphosphate product was increased according to the results of the lone phosphate control test in use: the orthophosphate procedure.

As expected, the demand for the polyphosphate product increased as the orthophosphate concentration in the reclaimed water went down. The orthophosphate test results clearly indicated the increase in demand. Some of the higher polyphosphate product dosage resulted in higher orthophosphate levels in the cooling water (as a result of hydrolysis of polyphosphate in the cooling water). So, the lone orthophosphate test results were increased when the polyphosphate product dosage was increased. Unfortunately, the orthophosphate test results alone, failed to show the level of "Total Phosphate" in the cooling water, which was necessary to permit the desired level of orthophosphate in the cooling water. Total Phosphate test results would have given this key information but that procedure was no longer part of the program. Therefore, while the orthophosphate test data indicated that all was well, the cooling water in fact was severely over-treated with polyphosphate.

This latent problem should have been anticipated and prevented by the technical service representatives of the refinery's water treatment chemical supplier, but it was not and, after several months of operations under these adverse conditions, inspections during a scheduled multi-unit turnaround revealed a severe heat exchanger fouling condition. The additional maintenance that the

Contact the Authors

David Daniels
512-407-3752
david_daniels@mmengineering.com

Gary A. Loretitsch
512-407-3765
gary_loretitsch@mmengineering.com

fouling required was costly and delayed production. Even worse, it was assumed that the heat exchangers of other units would be similarly affected with the potential of an unscheduled outage in the offing. Unscheduled shutdowns are an anathema to a refinery. But in this case, the refinery was anticipating one due to the false economy of taking a shortcut in testing using the "Pinks and Blues."

Before the problem was solved, it made the refinery question the value and even the feasibility of continuing its use of reclaimed water. Fortunately, the problem's root cause was properly determined and proper cooling water quality was promptly restored. Reclaimed water is a renewable source of fresh water for industry. It will become increasingly important as fresh water supplies continue to be stretched and shortages loom. It would have been a shame if the real benefits of reclaimed water would have been denied to the refinery over a misuse of the "Pinks and Blues."

M&M Engineering Associates, Inc. Will See You at These Conferences

HRSG User's Group
2008 Annual Conference & Exposition

Hilton Austin
500 East 4th Street
Austin , TX 78701
Monday, April 07, 2008 - Wednesday, April 09, 2008

Western Turbine Users, Inc.

2008 Annual Membership Meeting
Town and Country Resort & Convention Center
San Diego
April 6 - 9

Seminars and Workshops Attended

Ronald E. Munson, P.E. and Principal Engineer at M&M Engineering Associates, Inc., was invited to present *The Use of Advanced Ferritic Alloys in Steam Generation* at the Power-Gen International Conference held in New Orleans, Louisiana, in December 2007. For information on this or any other presentations by Ron Munson, please contact Ron at ron_munson@mmengineering.com.

In Memorial
Tony Lam

Chungtung Tony Lam was born in China in 1949. He immigrated to the US in 1978 and earned a Masters Degree from Cornell University in 1979. He founded Turbine Technology International after his graduation and was its President and Technical Manager at the time of his death. Tony developed the BLADE code for EPRI and was a renowned expert on rotating equipment analysis.

He is survived by his wife, SheWan; his mother Jin Zhu; his son, Arthur; his daughter, Grace.

Through the journey of life and career, you will meet many people…some you will forget, some you will remember, and a smaller group yet will become your friends. Tony Lam was such a person to me. Tony passed away on Christmas Day 2007. I had the honor of knowing Tony for 15 years. We worked together on analysis projects from opposite sides of the table, and on the same side of the Table. I have worked for Tony and have also had Tony work for me. One thing you could count on was it did not matter who was working for whom. Tony was consistent in his approach, his principles of integrity, and furthermore, he was generally right! He will be missed by me, and by the entire technical community.

Ronald E. Munson, P.E.
Vice President
M&M Engineering Associates, Inc.

***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.

For technical information, please contact:

David Daniels
(512) 407-3761
david_daniels@mmengineering.com

Ron Munson
(512) 407-3762
ron_munson@mmengineering.com

Karen Fuentes
(512) 407-3778
karen_fuentes@mmengineering.com

ENGINEERING ASSOCIATES, INC.

TEXAS • ILLINOIS • OREGON

www.mmengineering.com

__ Please add my name to your mailing list.

__ Please delete my name from your mailing list.

__ Please correct my information as listed below.

I prefer to receive this newsletter by ____ Email _____ Mail

Name: ____

Title: ____

Company: ____________________________________

Address: _____________________________________

City: ________________ State: _______ Zip: _______

Phone: ______________ Fax: ___________________

Email: _______________________________________

Comments on this issue: ________________________

____

____

____

Please send or fax this form to :

M&M Engineering Associates, Inc.
4616 W. Howard Lane Building 2, Suite 500
Austin, TX 78728-6302
Fax: (512) 407-3766

***the* Conduit**
M&M Engineering Associates, Inc.
4616 W. Howard Lane, Bldg. 2, # 500
Austin, TX 78728-6302