the **Conduit**

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INSIDE THIS ISSUE:

Chemical Treatments for Closed Loop Systems	5
Upcoming Events	9
Workshop—Fall Edition	10

PIN HOLE LEAKS IN TUBING

By: Karen T. Fuentes, P.E.
Sr. Principal Engineer

Pinhole leaks in tubing occur frequently and for a variety of reasons. Here are a few examples of conditions leading to pin hole leaks in tubes.

Under Deposit Corrosion

As the name implies, under deposit corrosion results when deposits are laid down on either the internal or external surface of a water-touched tube. Once a deposit is laid down on the tube surface the "chemistry" of the environment under the deposit can become significantly different to the general tube environment. It is this concentrating effect under the deposit that leads to pitting. The corrosion can be caused by a number of chemical species including caustic (caustic gouging), oxygen (oxygen pitting), and phosphate (phosphate gouging or acid phosphate corrosion). In water-containing piping and tubing in ambient or near ambient temperatures, microbiological deposits can also cause corrosion.

External deposits tend to collect in dead flow areas such as near baffle plates and tube sheets. Internal deposits tend to collect on the bottom of horizontal tubes, in the corners of the rifling of internally rifled tubes, at the liquid line in tubes that are only partially filled, in flow disruption areas such as bends, or areas of high heat flux.

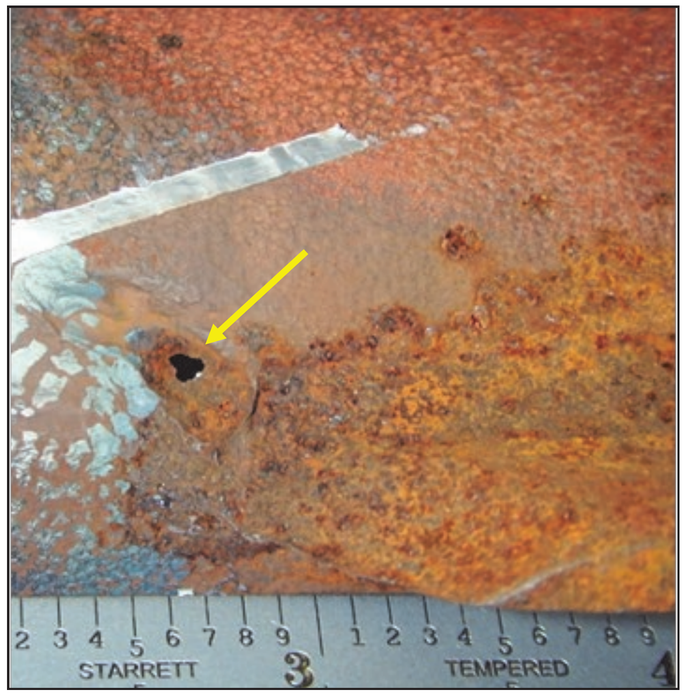

Figure 1. A small leak shown on the internal surface in the tube wall (arrow).

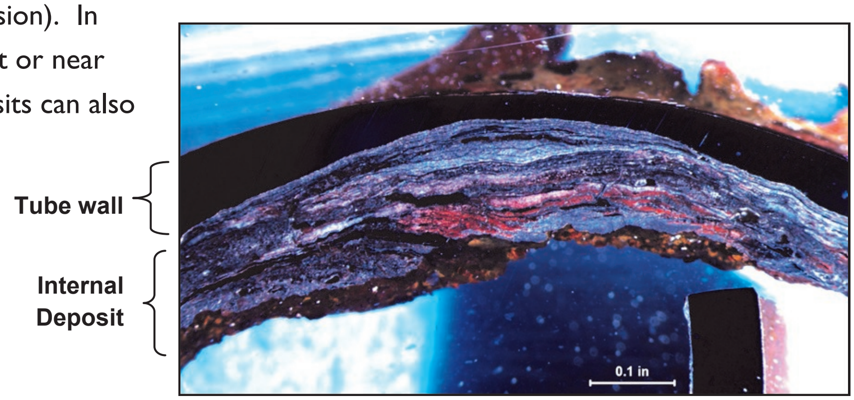

Figure 2. A cross section of tube shown in the area of the leak.

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Case Study 1

A waste heat boiler was having repeated tube failures. Examination showed that the tubes were failing due to under deposit corrosion (Figure 1 and Figure 2), specifically caustic gouging. There was broad smooth corrosion with little undercutting underneath a heavy, multi-layer deposit on the internal surface in localized areas. The deposit contained a significant amount of sodium. Normally, caustic is soluble and does not concentrate to significant levels under a deposit without the aid of high heat flux. At the hot spot, a fully nucleate boiling condition is not achieved. Once the deposit forms and heat creates the concentrating mechanism, if there is caustic in the boiler water, it can create under deposit corrosion by caustic gouging.

Microbiologically Influence Corrosion (MIC)

MIC is caused by bacterial activity that attacks metal. The bacteria either attacks the metal directly, consuming certain constituents of the alloy (example – iron utilizing bacteria), or they secrete acids which attack the material. In either instance, only the material directly under the colony is affected. In essence, MIC is a highly specialized form of under deposit corrosion with the bacteria colony or biofilm acting as the "deposit."

Most metal alloys used in industrial applications are susceptible to MIC, including copper, stainless steel, and carbon steel. (It should be noted that copper alloys are less susceptible to MIC as copper is a natural biocide.) Under certain conditions, colonies of bacteria form on the surface of the metal, typically in a circular pattern. Some mechanical and chemical cleaning methods have been developed to combat MIC, but the colonies can be difficult to remove. Additionally, once removed, the underlying pits become excellent sites for other types of under deposit corrosion as material tends to become "caught" in the pits.

Case Study 2

An office building was having repeated problems with leaks in their potable cold water line. The water was supplied from a well, but was passed through a water

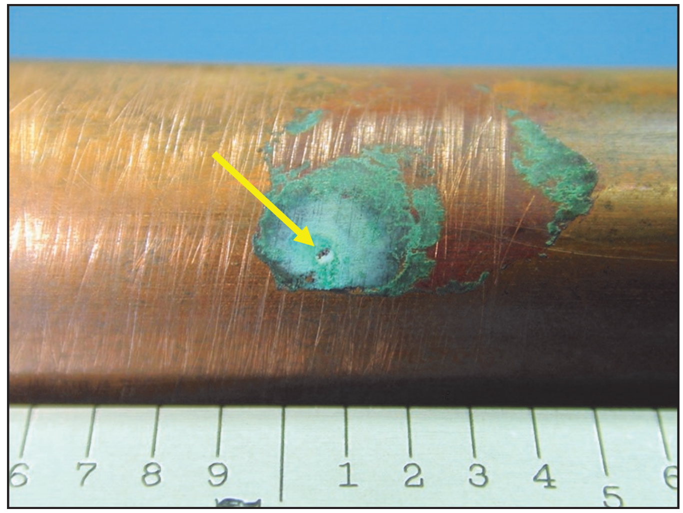

Figure 3. A leak shown in the cold water line on the external surface.

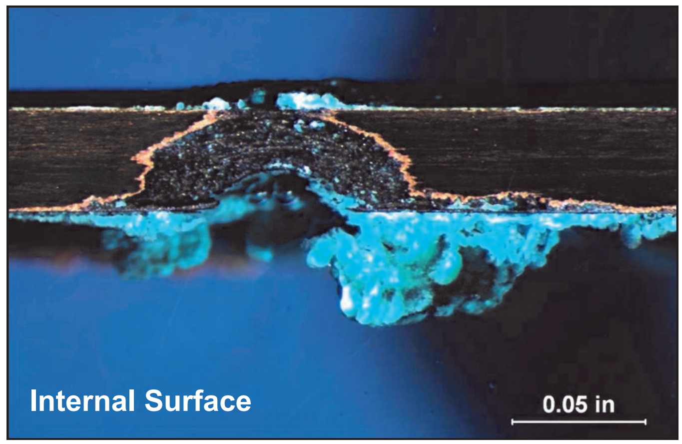

Figure 4. A cross section shown in the area of the leak.

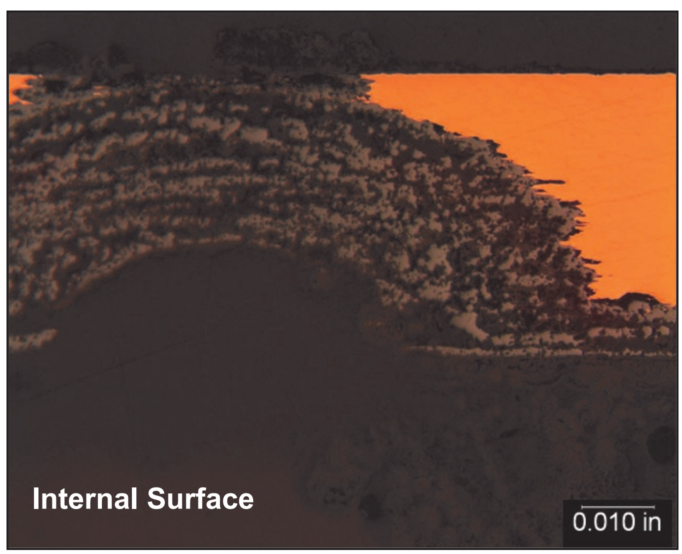

Figure 5. Deposits and lateral attack are characteristic of MIC.

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softener. The water was not chlorinated. The areas experiencing the leaks were lines with low flow or stagnant sections of the line. Examination showed that the leaks were due to microbiologically influenced corrosion (MIC) (Figure 3 through Figure 5).

Erosion

Erosion is the removal of material due to high velocity flow that wears away the tube material. It can remove significant amounts of material in relatively short periods of time. Erosion typically forms "horseshoe" shaped patterns with the most material removed near the arc of the horseshoe. This is the area which typically penetrates the tube wall resulting in a small leak. It is not until the tube is inspected internally that the extent of the erosion damage is observed. When erosion is assisted by corrosion, the mechanism is referred to as erosion-corrosion.

Case Study 3

A service contractor added a scale removal chemical (inhibited hydrochloric acid) to the cooling tower for the purpose of cleaning the condenser tubes in a centrifugal chiller, as well as the cooling tower and interconnected piping. The scale removal chemical was allowed to remain circulating in the system overnight instead of a few hours. Shortly after the scale removal, the chiller experienced severely leaking condenser tubes. The tubes were inspected using eddy current inspection method that showed tube wall loss and a pressure test of the tubes showed a significant number to tube leaks. Because of the extended period of exposure to the descaler, the inhibitor broke down and allowed erosion-corrosion of the tubes to occur (Figure 6 and Figure 7).

Dew-point Corrosion

Dew-point corrosion refers to the corrosion that occurs on tubing exposed to gases containing corrosives that reach their dew points (the temperature at which condensation of water entrained in the gases occurs). This is seen in tubing in systems such as economizers and reheaters that are recovering energy from combustion gases before they are released to the

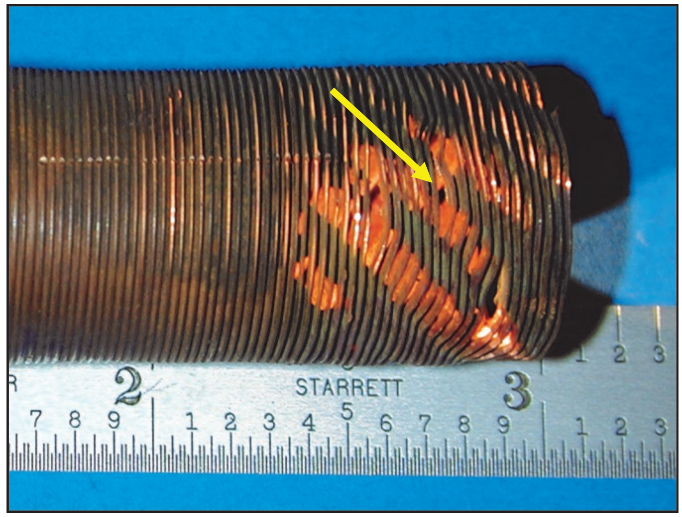

Figure 6. A leak shown in the externally finned tube.

Figure 7. Horseshoe-shaped divots are characteristic of erosion. In this example, corrosion also played a role.

atmosphere. As the last amounts of thermal energy are extracted from the gases, they cool and reach their dew points. The condensing water reacts with the corrosives, such as sulfur, in the gas stream to produce acids that corrode the tubing. Factors that affect the acid dew point are: fuel type, amount of excess oxygen, moisture level, tube surface temperature, air in-leakage, and catalysts.[1] Dew-point corrosion will cause general wastage of the tube wall but is typically manifested as a pinhole leak in the tube.

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[1] EPRI Technical Report: "Boiler and Heat Recovery Steam Generator Tube Failures, Theory and Practice," Volume 2, Water-Touched Tubes, No. 1023063, December 2011.

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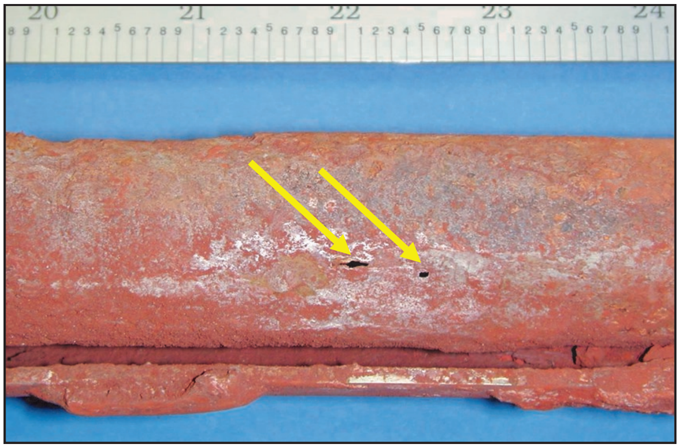

Figure 8. Image shows pin hole leaks in an economizer tube.

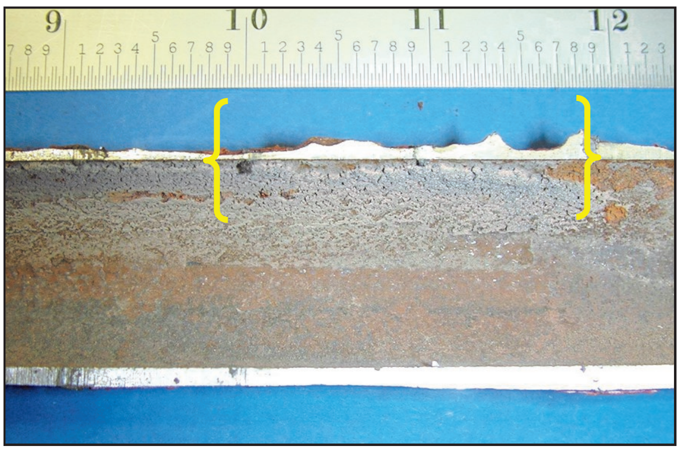

Figure 9. Image shows external wastage of tube in the leak area (bracket) viewed from the internal surface.

Case Study 4

A tube sample was removed for analysis after repeated pinhole leaks were experienced in the economizer from a coal burning, circulating fluidized bed boiler (Figure 8). After sectioning the tube, wastage of the tube wall was observed (Figure 9). Analysis of the external deposits identified primarily iron and oxygen (iron oxide), with some sulfur. A white layer of iron sulfate at the tube deposit interface is also typical of dew-point corrosion. White deposits were observed in the leak area.

The first temperature at which sulfuric acid condenses depends on the partial pressures of SO_3 and water vapor, and is usually around 250°F to 300°F. Coal firing may have a slightly lower dew point range (250°F - 285° F) because much of the ash contains alkaline compounds. The peak corrosion rate occurs at about 260°F. Excess oxygen is also an important factor as the higher the oxygen level in the combustion process, the more SO_2 will be converted to SO_3. By controlling excess oxygen to a maximum of 1 to 2%, it is possible to avoid the the formation of fully oxidized sulfur compounds and thereby reduce fouling and tube corrosion.

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In Memoriam

Arthur H. Tuthill, prominent chemical engineer from Blacksburg, Virginia, died February 10, 2015, at the age of 95. He graduated from the University of Virginia as a chemical engineer and earned his master's degree in metallurgy from the Carnegie Institute of Technology. He worked in corrosion engineering for Standard Oil, Valco Engineering, and International Nickel, and as a corrosion consultant for Tuthill Associates. Art also worked with M&M Engineering for many years. A prominent and specialized corrosion engineer, he authored more than 100 technical papers and received numerous awards in his field. His contributions to the fields of metallurgy and corrosion will assist us for years to come; he will be missed.

Chemical Treatments for Closed Loop Systems

By: David G. Daniels
Sr. Principal Scientist

Closed loop cooling systems are integral to the HVAC systems for offices, laboratories, production, and IT services. They are often in every occupied building, and run above suspended ceilings over offices, laboratories, and manufacturing areas, and through floors and conduits with other piping and electrical wiring. Leaks in these systems are more than just a nuisance or an increased maintenance cost; it can result in lost research, ruined or delayed products, inoperable computers, and lost time for key personnel.

In a closed loop system, oxygen pitting is the most common type of corrosion. In order for oxygen pitting to occur, there must first be a deposit which covers a portion of the metal surface, creating a differential between the oxygen content underneath the deposit and the oxygen content in the bulk water. The oxygen deficient area underneath the deposit becomes the anode, and the area around the deposit that is exposed to the bulk water becomes the cathode. This "big cathode, little anode" configuration causes concentrated and accelerated pitting in a confined area producing pinhole leaks.

There are two factors that can increase the rate of corrosion under the deposit. First is the concentration of chlorides either in the bulk water or underneath the deposit. The chlorides accelerate the electron transfer from the base metal to the bulk water, greatly accelerating the corrosion rate.

The second factor that can increase corrosion in a closed loop system is microbiological. If bacteria are allowed to propagate inside the closed loop system, they can create a "living" deposit that consists primarily of exo-polysaccharides and bacteria. The byproducts of bacterial respiration are often acidic, and respiration also consumes oxygen causing the base of the biofilm to be conducive to corrosion of the base metal. This further encourages some types of bacteria as they use the oxidized metal in their metabolism. This type of corrosion is so common that it has its own designation – microbiologically influenced corrosion (MIC).

It is very common for oxygen pitting and MIC to work together to corrode piping. Any area of piping that contains crevices, such as the space between threaded fittings, is an excellent area for general oxygen pitting and microbiologically influenced corrosion (MIC). So threaded fittings are very common areas for leaks.

Closed Loop Chemical Treatments

Sodium Nitrite

Sodium nitrite has been used for many years to prevent corrosion in a wide variety of closed loop systems. The mechanism is somewhat interesting in that the nitrite molecule itself is an oxidizer and prevents corrosion by causing a uniform layer of corrosion products on all carbon steel surfaces. Since it is an active oxidizer, as long as there is sufficient nitrite in the system, any area that begins to create an anode will quickly be oxidized.

However, if there is insufficient nitrite in the chilled water loop, the nitrite corrosion inhibitor can actually accelerate the rate of corrosion. The general guidelines for nitrite-based treatments are for a minimum of 700 ppm of nitrite.

Nitrite treatments traditionally also contain pH buffers (caustic and sodium borate) to maintain an alkaline pH, which is conducive to minimizing corrosion in carbon steel. If there is copper in the closed loop system, tolytriazole (TTA) is added to the treatment to maintain a protective chemical layer on top of the exposed copper metal surfaces.

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Nitrite treatments have a concern in that the nitrite molecule is the source of energy for certain types of bacteria. If the closed loop system becomes contaminated with these bacteria, the nitrite level can decrease very rapidly leading to corrosion. The nitrite will first be converted to nitrate by nitrifying bacteria and then denitrifying bacteria will convert nitrate to ammonia. Ammonia is very corrosive to copper.

Furthermore, the bacteria generate biofilms which prevent the nitrite treatment from accessing the area under the deposit. Adding more nitrite only further accelerates the reproduction of the bacteria making the problem worse. Systems using nitrite should be regularly tested for the presence of bacteria. In some systems, non-oxidizing biocides such as glutaraldehyde or isothiazoline are added to the treatment to prevent bacterial growth. Some closed loop systems have also used an oxidizing biocide, chlorine dioxide, to eliminate bacterial contamination.

Sodium Molybdate

Molybdate is generally classified as an anodic oxidizing inhibitor. Molybdate works in conjunction with the dissolved oxygen in the water to form a protective ferric-molybdate complex on the steel. Molybdate is also thought to create a negative surface charge on the outer portion of the protective layer making it more impervious to aggressive chloride and sulfate.

Molybdate treatments cannot be used where there is a significant hardness in the water (>500 ppm as $CaCO_3$) (the presence of calcium and magnesium measured as 7500 ppm a $CaCO_3$). Molybdate treatment levels can be anywhere between 200 – 800 ppm as molybdate depending on the other constituents of the water such as sulfate and chloride. Closed loop systems that use demineralized water makeup would tend to be on the lower end of this range.

The world supply of molybdate tends to be concentrated in areas of historical political unrest. Therefore, over the years molybdate prices have varied dramatically, which can in turn make molybdate treatment competitive with nitrite, or far more expensive.

Ironically, in closed loop systems that are very tight, dissolved oxygen levels can drop and thus minimize the effectiveness of a molybdate treatment (which requires dissolved oxygen to form a passive layer). Experts recommend a minimum of one ppm of dissolved oxygen in molybdate-treated systems.

Silicates

Silicates were the first chemical corrosion protection system used in water systems. Silicates are also classified as anodic inhibitors similar to molybdate. However, the protection mechanism consists more of the formation of a filming layer of silicates on top of the carbon steel than an interaction directly with the ferrous metal. The silicate layer forms slowly (weeks). Silicates can provide corrosion protection for copper and other metals, as well as carbon steel.

Silicates do not act as a nutrient for biological growth, which is an advantage they have over nitrites. Silica deposition can occur if the system is over-treated, or in the presence of high concentrations of calcium and magnesium. The typical treatment level is between 50 and 100 ppm when used as a stand-alone treatment. Silicates may also be used in conjunction with other treatments.

Polymer Treatments

Polymers have been used for many years to prevent scale and corrosion product accumulations in cooling towers and low pressure boilers. They are also now used in closed loop systems. The polymer acts as a dispersant for any corrosion products or scale that might form, so it "prevents corrosion" by keeping the surface clean and ensuring that any dissolved oxygen in the water attacks all surfaces evenly. This produces a general, but overall low level of corrosion. Current understanding of the mechanism is that polymers are a passive treatment—in other words; they do not react with or cause any active chemical change to the surface of the metal to create a passive layer (unlike nitrite and molybdate). Instead, it presumes that if it can keep the surface clean, a uniform oxide layer will form and pitting corrosion will be controlled.

In addition to the polymer, these treatments typically contain pH buffers (caustic and borate) and may include TTA for copper corrosion protection.

One of the advantages of this treatment is that it is thought to be very environmentally benign. The polymer in the treatment can be found in a number of consumer products and has been used in the water treatment industry for many years.

Toxicity

As far as environmental toxicity, sodium nitrite has the lowest LD_{50} (rat) of the treatments discussed here. In order from most to least toxic they are:
Nitrite > Silicate > Molybdate > Polymer.

Table 1. Toxicity of Closed Loop Cooling Water Treatments[1]

Primary Chemical Constituent	LD_{50} (rat) (mg/kg)
Nitrite	180
Silicate	800
Molybdate	4,233
Polymer	>5000

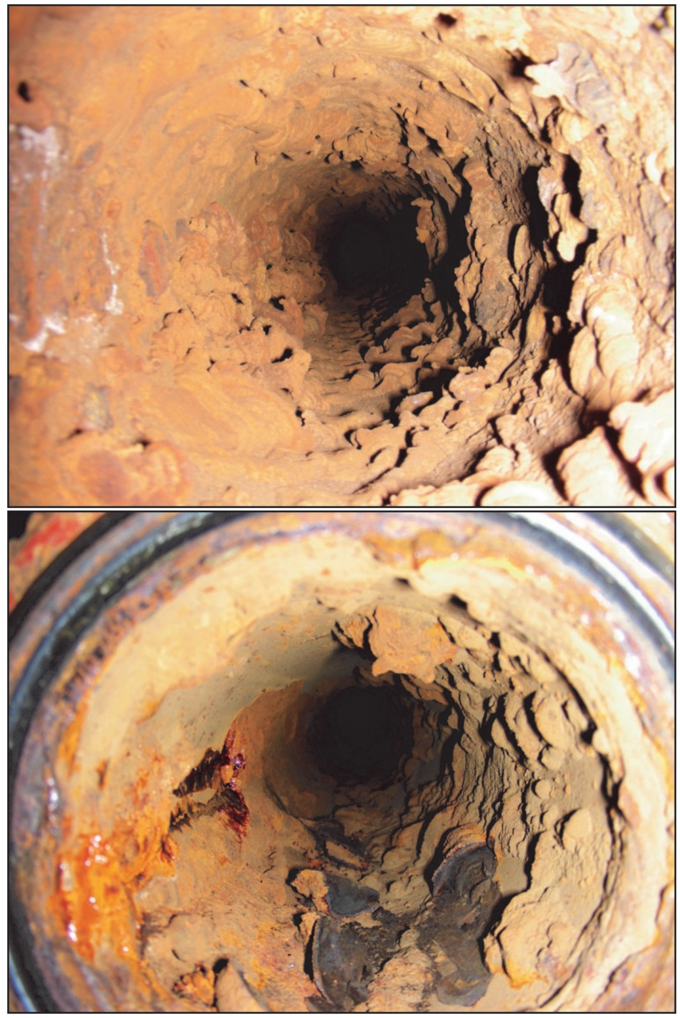

Figure 1. Typical corrosion of chilled water piping at the Case Study 1 facility.

Case Study 1

A sporting facility located in a southern state had a natural grass field. The movable roof was open to the sun during the day and closed in the afternoon, approximately three hours before game time. At that point, the massive air handling units were turned on to reduce the temperature and humidity in the entire stadium to a comfortable level before the game started. There were over seven miles of chilled water piping in the stadium.

After approximately twenty (20) leaks had occurred in the chilled water loops, M&M Engineering was called in to assess the damage and make recommendations.

We determined that there was significant oxygen pitting throughout the carbon steel piping system that was responsible for the leaks (Figure 1). The investigation found that the chemical vendor had recommended a molybdate-based chilled water treatment. However, due to the expense of the molybdate during this time (molybdate prices had skyrocketed), the vendor chose to reduce the amount of molybdate treatment to levels well below what is considered normal. The system also had some leakage which reduced the concentration and increased treatment costs further.

In addition to conventional oxygen pitting corrosion, there was a significant presence of sulfate reducing bacteria (SRB), which were contributing to the corrosion rate.

As a result of the corrosion, much of the 4-inch diameter or smaller steel piping of the chilled water system had to be replaced by copper pipe, copper alloy fittings and valves, and new insulation.

It is not only the corrosion of the piping that created

(Continued on page 8)

[1] Rey S., Molybdate and Non-molybdate Options for Closed Systems—Part II, The Analyst.

problems in the chilled water loop. Corrosion products broke off and accumulated in narrow portions of the system, behind valves, and plugged off heat exchangers that affected the HVAC system. In this particular system, the air handling units (AHUs) (Figure 2) contained enough deposits to prevent proper operation. Remediation options included mechanical cleaning, chemical cleaning, and complete replacement of the AHUs.

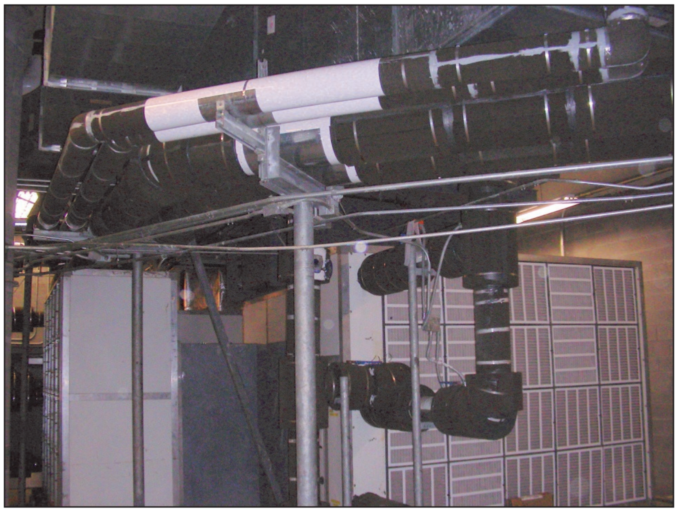

Figure 2. Typical air handling unit (ACU) at the Case Study 1 facility.

The pump seals are another area where corrosion deposits accumulated. The abrasive nature of the corrosion products destroyed the seals causing additional loss of seal and water, as well as leaking.

Other less obvious problems were also found including higher than design energy costs associated with the increased resistance to flow, which the recirculating pump motors must overcome.

It should be emphasized that in this case, the corrosion was the result of an inadequate water treatment; not the complete absence of it. Also, the corrosion occurred relatively quickly, but did not manifest itself until it progressed so far that significant amounts of the piping and equipment had to be cleaned and/or replaced (Figure 3).

Case Study 2

A large hospital outpatient center had just been completed in a large metropolitan area. Over 700 HVAC

Figure 3. The replacement of piping was already underway when we arrived at the Case Study 1 facility.

heat exchangers were installed to carry chilled and hot water to each room in the facility. The system was very complex and included coils and reheater elements controlled to ensure that the temperature and humidity in the various offices, recovery areas, and operating rooms were properly regulated. In this particular case, the failures occurred in the hot water loop.

Our investigation found that during construction, the hot water loops had been cleaned of construction debris and left filled with untreated water for testing. Delays resulted in the water remaining stagnant in the system for some time without any additional treatment or monitoring. When it was finally put into service, the chemical company had difficulty establishing and maintaining the passive nitrite chemistry. There were long periods where the nitrite level essentially dropped to zero.

Approximately a year later, the first leak appeared. This was quickly followed by 11 more leaks. Eventually, the leak rate became so significant (inspection found 147 heat exchangers that showed signs of leaking) (Figure 4) that the construction firm agreed to replace all 747 exchangers. In this case, there was a complete lack of treatment during the construction and subsequent commissioning phase. When treatment was eventually started, corrosion already established in the system made it

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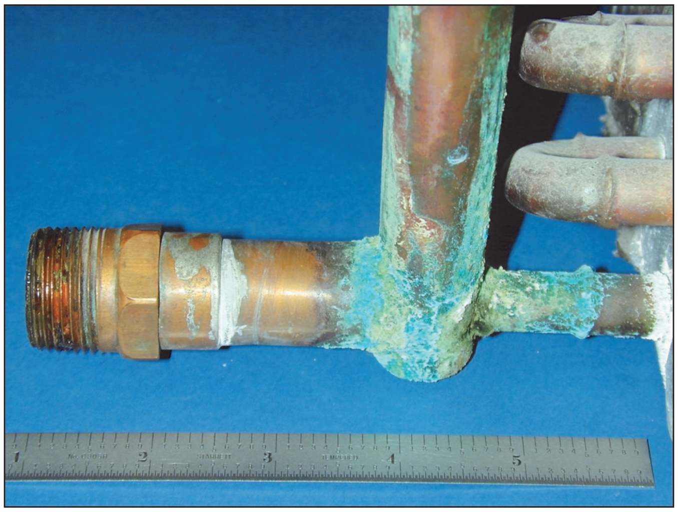

Figure 4. Corrosion of an unprotected closed loop system after approximately one year.

very difficult to maintain. Corrosion products in the system required frequent flushing to prevent damage to the pumps and heat exchangers. The potential for even minor leaks to damage expensive equipment, offices, and sterile spaces such as operating rooms made the wholesale replacement of all damaged equipment the only acceptable option at a significant cost to the contractor and disruption to the facility.

Summary

As the two case studies above show, corrosion in closed loop systems can occur rapidly (one to two years). Often the corrosion in the system goes undetected until it is so widespread that large sections of piping have to be replaced. Once the corrosion mechanisms have started, it is difficult to regain control and remove corrosion products. Closed loop cooling systems are meant to remain "closed," with very little makeup and no leaks or spills. Properly treated with corrosion inhibitors and maintained, systems can operate for years with no appreciable leaking.

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Upcoming Events

April 26-May 1, 2015
ASME Boiler Code Week
Colorado Springs, Colorado

June 2-4, 2015
35th Annual Electric Utility Chemistry Workshop
Champaign, Illinois

September 15-16, 2015
M&M Engineering Associates, Inc.
4th Annual (Fall Edition)
Preventing Failures in Steam Generating Equipment
Leander, Texas

October 13-15, 2015
EPRI International Conference of Corrosion Control in Power Plants
San Diego, California

November 15-19, 2015
76th Annual International Water Conference
Orlando, Florida

Visit our News & Events page for more details:
mmengineering.com/news-events/

M&M ENGINEERING ASSOCIATES, INC.

Preventing Failures in Steam Generating Equipment

September 15-16, 2015 — Leander, Texas

M&M Engineering will host a Fall Edition of their 4th annual workshop for producers of steam, be it used in power or process applications. The two day workshop focuses 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.

Seating is limited - register TODAY!

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

Day 2

- Introduction to Failure Analysis
- Failure Investigation Principles for Combustion Turbines
- Basic Steam 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

* (sessions are subject to change)

The registration fee for this two day event is $750 (continental breakfast and lunch are included).
The registration deadline is August 14, 2015*. For details, and to register online, visit:

http://mmengineering.com/events/event/4th-annual-preventing-failures-steam-generating-equipment-workshop-fall-edition/

Or contact Lalena Kelly by phone or email for further information:

(512) 407-3775 or Lalena_Kelly@mmengineering.com

Event Location: 1815 S. Highway 183, Leander, Texas 78641

*Subject to a minimum number of attendees. Once registered, attendees should confirm workshop before making travel arrangements.

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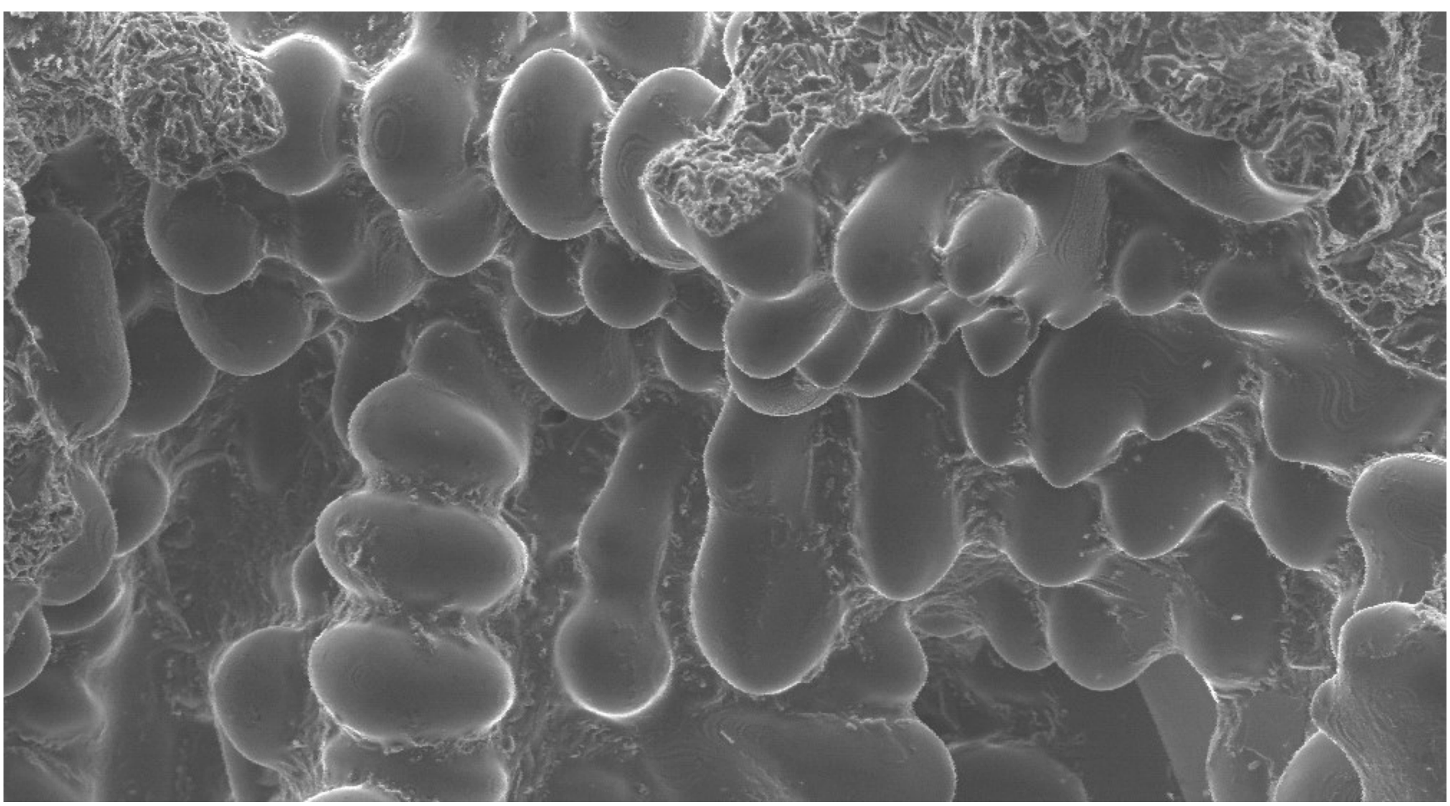

Spring has sprung! Pollen or Casting Voids in Aluminum?