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Monitoring Corrosion Rates in Cooling Water

By **K. Anthony (Tony) Selby**

The predominant piping material in cooling water systems is unlined carbon steel. Copper-bearing alloys such as Admiralty brass (C44300), or 90-10 copper-nickel (C70610) are very common for heat exchangers and condensers. Of course, there are many variations. Piping may be lined with carbon steel, cement, or plastic. Condenser and heat exchanger tubing may also be 304 or 316 stainless steel, higher grades of stainless steel, or titanium.

Unlined carbon steel, and the more common copper materials, may corrode when handling cooling waters. The corrosion can be exacerbated by some of the chemicals used for inorganic mineral scaling and microbiological control. Sulfuric acid may be used to reduce the pH of water in order to control mineral scaling. This can increase the rate of corrosion of system materials, especially carbon steel. Chlorine compounds (gaseous chlorine, sodium hypochlorite, etc.) are used to control microbiological growth. These oxidizing biocides also increase corrosion of carbon steel and copper alloys.

Why Monitor Corrosion Rates

Corrosion rate monitoring can be used to:

- (1) estimate baseline corrosion rates,
- (2) evaluate the impact of corrosion causing chemical on system materials,
- (3) determine the effectiveness of chemicals added to reduce corrosion (corrosion inhibitors).

Corrosion rate monitoring can be performed by either weight loss or electrochemical methods. Weight loss methods are described in ASTM Method D-2688 (Volume 11.01). Electrochemical methods are described in ASTM Method G-96 (Volume 03.02).

It should be noted that no method of measuring corrosion rates will exactly mimic the conditions in an actual system. However, there is much valuable information to be learned.

Common Weight Loss Methods

The most common method of corrosion rate monitoring consists of routing a bypass stream of cooling water through a "corrosion coupon rack" (Figure 1.) containing



Figure 1. Corrosion Coupon Rack.



Figure 2. Coupon Holders.

pre-weighed metal specimens (corrosion coupons). This particular design has the advantage of utilizing clear plastic tubing that allows observation of the condition of the coupon. The design also incorporates a flow-measuring device (rotameter) so that adequate flow through the corrosion coupon rack can be confirmed. In addition to bypass corrosion coupon racks, there are coupon holders (Figure 2) that allow

the corrosion coupons to be inserted directly into the flowing process stream and correctly orientated.

The corrosion coupon is prepared to a specified surface finish and weighed to four decimal places. After exposure, it is cleaned and reweighed. The exposed surface area, metal density and exposure time are used to calculate a corrosion rate in terms of mils/year (mpy) or millimeters/year (1-mpy = 0.0254-mm/year)

Corrosion Coupon Metallurgy

The metallurgy of the corrosion coupons used should almost always match, as closely as possible, the metallurgy (at least the most susceptible metallurgy) in the system. For example, if the heat exchangers contain copper tubes, the corrosion coupon should be copper (e.g., CDA-110) and not a brass or copper-nickel alloy. These are likely to have very different corrosion characteristics than the metal of interest aluminum coupons are sometimes used to detect copper throw.

Maintain Adequate Flow

Adequate flow is critical in order to obtain consistent and realistic results. ASTM suggests that the flow rate through the corrosion coupon rack be set to approximate the velocity in the piping of interest and that this is normally in the range of 2 feet to 6 feet per second. This would be approximately 3-gpm to 9-gpm in a corrosion coupon rack constructed of 3/4-inch pipe and 5-gpm to 15-gpm in a rack constructed of 1-inch pipe. In the author's experience, velocities at the low end of the ASTM specified range may not be sufficient to achieve consistent results.

Figures 3A and 3B show both sides of the same corrosion coupon. The corrosion is minimal on one side of the coupon (Figure 3A) and heavy on the other side of the coupon (Figure 3B). This type of corrosion pattern is usually an indicator of inadequate flow through the corrosion coupon rack.

Coupon Exposure Duration

When a new corrosion coupon is installed, the metal surface is "fresh" and readily susceptible to corrosion. The initial corrosion rate will be high until a protective oxide coating is formed on the surface. As the exposure of the coupon continues the actual corrosion rate decreases over time.

The exposure period selected depends on the purpose of the

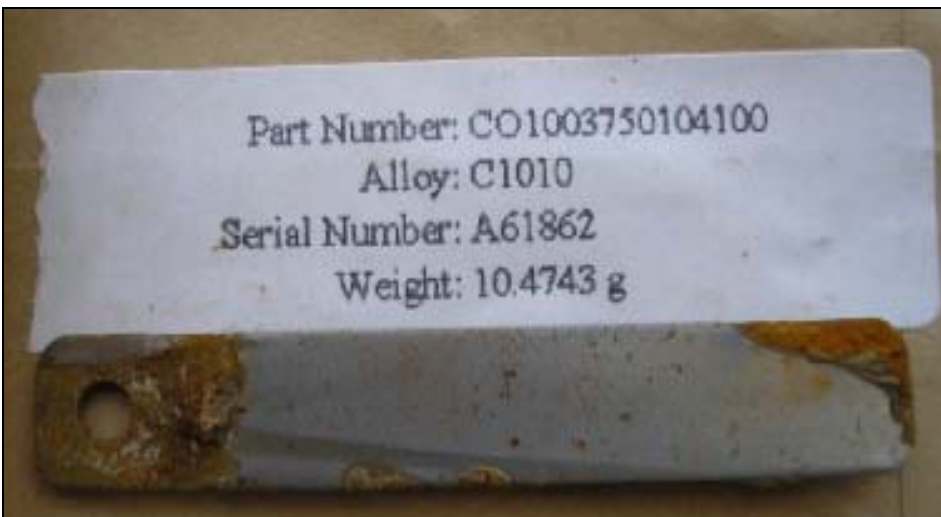


Figure 3A. Side of Corrosion Coupon with Minimal Corrosion.



Figure 3B. Side of Corrosion Coupon with Heavy Corrosion.

monitoring program. For general long-term monitoring of corrosion rates, a 90-day exposure period is often used. This is long enough to offset the impact of the initial high corrosion rate but short enough to detect fluctuating rates due to changes in system conditions or system upsets. An advantageous approach is to have three corrosion coupons of a particular metallurgy installed in the monitoring system. Each 30 days a coupon that has been exposed for 90 days is removed.

If the purpose of corrosion monitoring is to determine the impact of a change in corrosion inhibitors, a shorter exposure duration might be used. Here the purpose is to observe changes in relative corrosion rates and

not to assess an overall average.

Corrosion Rate Assessment

There is no single standard that determines what is an acceptable corrosion rate versus an unacceptable one. For one thing, it depends on the type of system being monitored. Higher corrosion rates can be tolerated in a cooling tower system than in a closed-loop cooling system. This is because much of the corrosion product generated in a cooling tower system will be removed from the system with the cooling tower blowdown.

Figures 4A, 4B and 4C show carbon steel corrosion coupons from different systems after 90 days exposure (after cleaning). The

measured corrosion rate of the coupon shown in Figure 4A was about 1-mpy. There is little observable corrosion attack. The corrosion rate of the coupon shown in Figure 4B was approximately 3-mpy. The impact of corrosion is visible. The corrosion rate of the coupon shown in Figure 4C was approximately 13-mpy. The impact of corrosion is very visible.

For carbon steel corrosion coupons in open re-circulating (cooling tower) systems, a corrosion rate less than 2-mpy would typically be considered "good". Corrosion rates for copper or copper alloys are usually much lower. First of all, copper alloys have better natural corrosion resistance than carbon steel. Secondly, these materials are often used in heat exchanger tubes that are much thinner than carbon steel piping.

Electrochemical Methods

There are also electrochemical methods used to determine corrosion rates. These include linear polarization resistance (LPR), electrical resistance (ER), and electrochemical noise (ECN). The most common of these is linear polarization resistance.

The LPR technique applies a small potential to a test electrode, typically about 10-mV. After a short delay to allow the current to stabilize, the current density is measured. The ratio of the potential shift and the resulting current density is equal to the polarization resistance, which is related to the corrosion rate.

The actual corrosion rate as measured by LPR may approximate the corrosion rate measured by a weight loss technique but sometimes the correlation is poor. However, there are many advantages to LPR corrosion rate monitoring. Because LPR takes measurements over short time periods, it is easy to determine trends. For example, LPR can be used to determine the impact of chemical injection (e.g. , chlorination) on short-term corrosion rates. It can also be used to quickly determine the

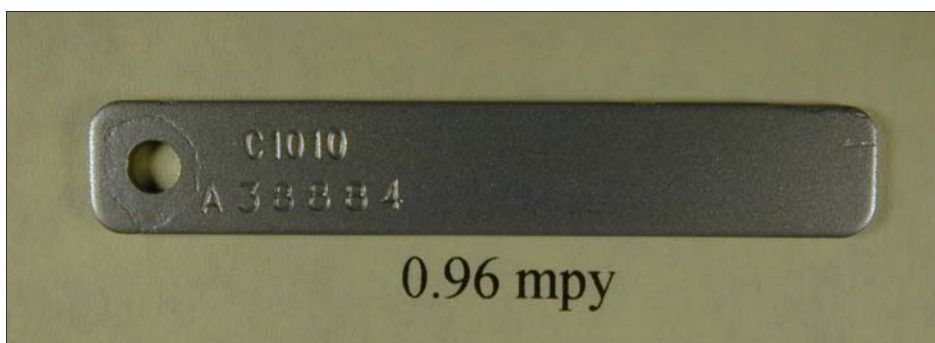


Figure 4A. Coupon with Approximately 1-mpy Corrosion Rate.

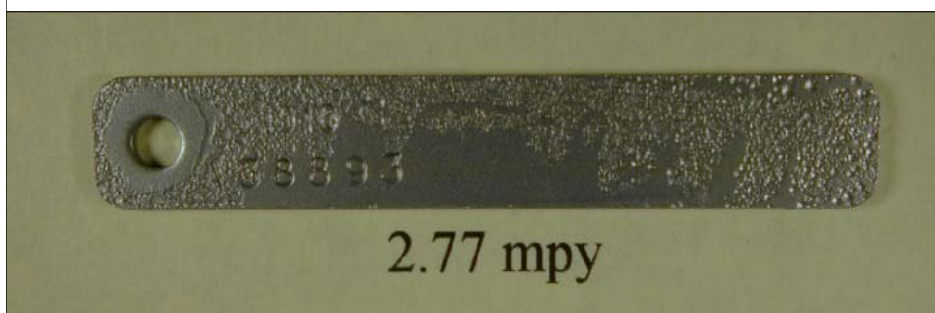


Figure 4B. Coupon with Approximately 3-mpy Corrosion Rate.

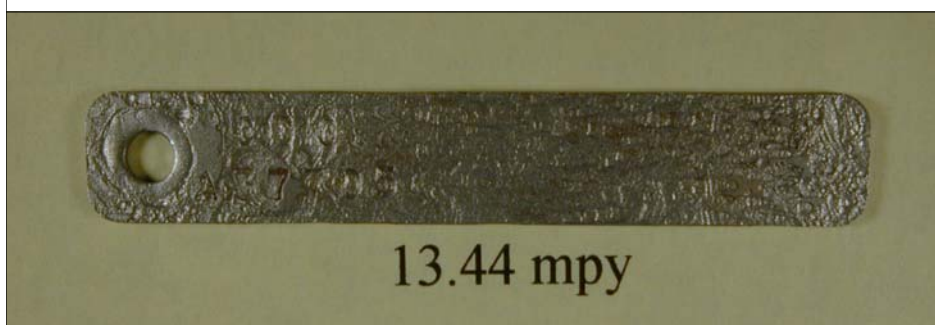


Figure 4C. Coupon with Approximately 13-mpy Corrosion Rate.

effectiveness of a corrosion inhibitor under test conditions. With LPR, this can be done in a matter of hours whereas a corrosion coupon would require exposure for a period of seven days to accomplish the same task.

LPR instruments range from a simple hand-held, single-channel instrument to panel-mounted, multi-channel units with dataloggers. While an instrument costs more than the equipment for weight loss measurements, the versatility and convenience of the electrochemical method often make this approach cost effective. Instruments can range in cost from \$1,000 to \$2,000. Probes are reasonable in cost, and electrodes last for six to twelve months.

The electrical resistance (ER) technique is based on the fact that the resistance of a piece of wire will change as it corrodes and its diameter decreases. Monitoring utilizing ER is less common than LPR in cooling water systems., more common in petroleum processes and pipelines.

Electrochemical noise (ECN) is a newer technique that can measure pitting rates as well as general corrosion. Electrochemical noise corrosion monitoring derives information on the corrosion rate and the mechanism from naturally occurring fluctuations of potential and current. A great deal of electronic data is produced which must be analyzed by computer to generate useful corrosion rate data.

Corrosion Rate Monitoring Limitations

No method of measuring corrosion rates will exactly mimic the conditions in an actual system. Corrosion coupons have a clean and highly sensitive surface. Piping and heat exchanger tubing, on the other hand, have a mature oxide film on the surface that impacts the corrosion characteristics. A fresh corrosion coupon is often a “worst case” situation because the sensitive surface will corrode more quickly than a surface with a mature oxide film.

Heat transfer can be a factor in a real system. There is no heat transfer for an exposed coupon or LPP, R or EN electrode.

Corrosion coupon results represent an average corrosion rate. In reality, corrosion seldom occurs evenly overtime across the metal surface. However, coupons can be used to qualitatively assess localized corrosion. Likewise, electrochemical methods typically yield average corrosion rates although some methods can provide or measure an indication of pitting corrosion.

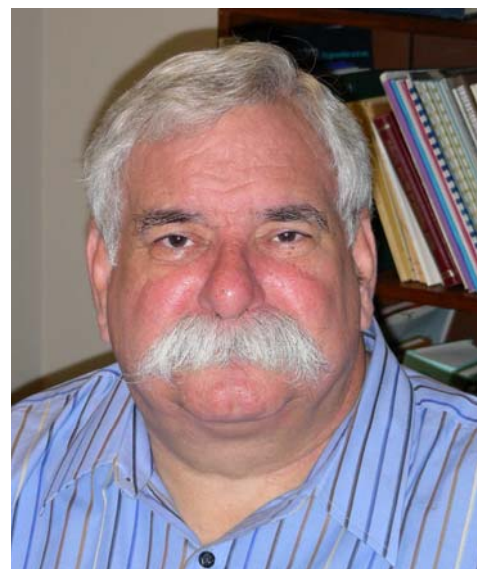
Corrosion rate monitoring methods generally will provide insight into the relative corrosiveness of a cooling water supply. They also provide general information about the effectiveness of corrosion inhibitors or information about the impact of corrosive additives such as chlorine or acids.

Gary A. Loretitsch Joins M&M Engineering

Gary A. Loretitsch has joined M&M Engineering as a Principal Scientist specializing in water treatment technologies. He was formerly a Vice President and Senior Consultant with Puckorius & Associates, Inc. He earned his BS degree from Fenn College of Engineering, Cleveland, OH and his MBA from the University of New Haven, New Haven, CT.

Gary has more than 40 years of practical experience in water and wastewater treatment technologies, including the design, application and management of industrial water treatment chemical products and water conditioning equipment systems.

He has worked closely with many potable water and wastewater utilities to facilitate the reclamation of wastewater and its reuse in power plants and industrial plants, especially oil refineries.



Oxygen Pitting and the Importance of Magnetite Film Maintenance in Low Pressure Boiler Water

By Gary A. Loretitsch

Oxygen pitting is one of the most frequent corrosion mechanisms identified in low pressure boilers. Once initiated, oxygen pitting is difficult to stop (Figure 1.). Pitting leads directly to tube penetration and failure of the boiler. Most corrosion mechanisms require very specific conditions—this is true for oxygen pitting. Combinations of two or more of the following conditions are usually required for significant damage to occur.

- Dissolved oxygen in the boiler water or in the boiler feedwater.
- Improper cleaning and passivation of new, repaired or re-tubed boilers .
- Loss of portions of the protective magnetite layer .
- Low boiler water alkalinity.
- Low or intermittent oxygen scavenger concentrations .
- Deposits delaying or preventing repassivation.

The terms *passivation* and *repassivation*, as they pertain to boiler water side steel, describe the reduction of hematite to magnetite one means by which a protective oxide film is created. Oxygen adversely affects the quality of a natural magnetite film and causes the formation of non-protective porous oxides such as hematite. In the absence of oxygen, magnetite gradually forms as a highly adherent, tightly bonded, protective coating on boiler surfaces. Higher pressure/temperature boilers can develop this magnetite layer directly from the reaction of the steel with

water. Lower pressure/temperature boilers require a consistently high hydrate alkalinity level for the magnetite layer to form and to be repaired/maintained as a protective film. For the purposes of this discussion, “low pressure” boilers are those operating at or below 450-psig. These boilers and their higher pressure counterparts are particularly prone to oxygen pitting when they operate at loads far below capacity, operate intermittently, and cycle frequently.



Figure No.1. Oxygen Pitting in Steam Drum.

Oxygen pits are rather easily identified by their appearance (Figure 2). In fact, a close observation of a representative sample of several oxygen pits can often reveal whether the pitting is active or not. When active oxygen pits are carefully rinsed out with plain water, shiny, unpassivated steel can be seen at the bottom of the pits. The bottoms of inactive pits, on the other hand, will appear dull and coated with a grey-to-black magnetite film.

If there is doubt about the cause of the pitting, SEM-EDX analysis of a tube sample with typical pits can confirm the corrosion mechanism (or mechanisms) involved by identifying ion species in the

bottom of a pit, precisely where the corrosion is taking place. However, EDX data must be carefully interpreted because the mineral content of the boiler water significantly influences the type and concentration of ions that migrate to the points of attack.

For example, sulfate ion is often a predominant anionic species in low pressure boiler water. Some of the sulfate is indigenous to the water supply—some is added when the water is treated by a sodium sulfite-based oxygen scavenger, which becomes sodium–sulfate when it reacts with oxygen. In a typical corrosion cell, whether or not the corrosion rate is accelerated by the presence of oxygen, anions migrate from the water to the anode where iron is moving into solution. Hydrate, sulfate, and chloride all tend to participate in this part of the corrosion reaction. As a predominant anion in the boiler water, particularly when hydrate concentration is low or nil and chloride concentrations are relatively low, sulfate ion can migrate to the anode and react to form iron sulfate. In this example, the sulfate ion is neither a causative agent nor is it a product of the corrosion mechanism, per se.

When corrosion of steel occurs, positively-charged iron atoms (primarily divalent Fe) are released



Figure 2. Typical Oxygen Pit.

from the metal surface. If these ions are trapped at the metal surface (such as beneath a deposit), a net positive charge develops at that location. At some point, the charge buildup serves to limit further release of iron ions from the metal, thus polarizing the surface and slowing the corrosion rate. The positive charge attracts negative ions in solution, such as sulfate or chloride, if a pathway exists for migration through the deposit. As the anions neutralize the charge, the metal surface is depolarized, and corrosion proceeds. Chloride is most commonly associated with this process, because it is smaller than sulfate and can migrate through smaller crevices at a faster rate. However, if sulfate is the predominant anion present, it will also neutralize positive charges. Under these circumstances, boiler corrosion products can contain sulfate without the sulfate having been the cause of the corrosion.

A good example of the high cost of oxygen pitting occurred at one US refinery. The refinery operates waste heat boilers at three pressures: 25-psig, 45-psig, and 150-psig. They also have conventional fuel-fired boilers at 450-psig and power boilers at 850-psig. None of these boilers had suffered any significant waterside corrosion damage for many years of service. That is, until a series of waste heat boiler failures began to interfere with production.

The refinery's preliminary investigation revealed that the boiler tube corrosion and perforation problem appeared to be limited to only the lower pressure waste heat boilers. Subsequent analysis of tube samples exhibiting pits identified sulfate ion as the primary ionic species in the

pits. This led the refinery staff to speculate (erroneously, as it turns out) that the cause of pitting was an unidentified heat exchanger leak causing intermittent contamination of boiler feedwater with a corrosive sulfur species such as sulfide ion.

A consultant was called in to do a complete metallographic examination of the pits in several typical damaged tube samples. His findings confirmed the presence of sulfate within the pits and further fueled the refinery's suspicion about sulfide contamination. He was unable to help with the identification of the source of the suspected leak.

At this point, the refinery was left with the prospect of continued chronic waste heat boiler failures at least until such time as the leaking heat exchanger could be identified and repaired. When more boiler failures occurred, as expected, the boilers were taken to the inspection and repair pad where the pitting damage could be shown to anyone with an interest in solving the problem. Soon an independent water treatment consultant on other business in the refinery was shown the damaged tubes. This experience enabled him to identify the metal loss as "common oxygen pitting".

He also found that the refinery had switched from testing alkalinity to testing boiler pH. The pH of the cooled boiler sample was affected by the amine, which gave an artificially high pH reading.

In most low pressure boiler systems, the excess hydrate alkalinity is maintained at a level high enough to relegate the influence of amine alkalinity to insignificance. In boilers operating with low levels of hydrate alkalinity, the effect of amine on pH cannot be ignored.

The refinery's low pressure boilers had been in jeopardy for several years. The problem began when alkalinity titrations and other boiler water tests, such as sulfite residual, were discontinued or curtailed.

Dependence on pH measurements alone rather than alkalinity titrations permitted low hydrate alkalinity levels in the low pressure boiler water, at least intermittently. Insufficient hydrate alkalinity prevented the establishment and maintenance of a continuous magnetite corrosion barrier on the steel tubes of the low pressure boilers. This condition left the tubes susceptible to several corrosion mechanisms, including under deposit acidic and oxygen accelerated pitting. Further boiler damage was prevented by modifying the boiler water testing and control program to monitor more frequently and more comprehensively the hydrate alkalinity and oxygen scavenger residuals in all of the low pressure boilers. Since the boiler feedwater and boiler water testing and control program was corrected as recommended, there have been no further waste heat boiler failures due to oxygen pitting/perforation.


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