

Boiler Chemistry Management Using Coordinated Approach of Chemicals, Membranes and Online Monitoring

Authors:

Rajendra Prasad Kalakodimi, Lead Technologist, and Mel J. Esmacher, Engineering Manager, GE Water & Process Technologies

Abstract

Managing boiler water chemistry plays a major role in avoiding several forms of boiler tube failure (BTF) because of corrosion and related steam system damage. In the first part of this report, a case study will be presented that detail the types of failures that can occur as a consequence of exceeding prescribed contaminant limits. In the second part we will discuss implementing RO treatment of boiler makeup water, which can substantially improve water quality, and enhance steam purity and often eliminate boiler system fouling and corrosion problems. Internal treatment with a good chemicals control approach along with a suitable polymeric dispersant program will also be discussed. Light will also be thrown at a new TOC Analyzer for Boiler Water Monitoring.

Introduction

During the last decade, General Electric Company created a water and process platform called Water & Process Technologies. This business brings together leading companies in the water industry. The integration of these businesses has created a powerful force with a range of cutting edge technologies to help customers improve performance and reduce costs in a broad range of applications. This wide range of technologies provides an interesting challenge when trying to find the best series of unit operations to address an application. This is particularly true in view of the need to treat feed waters that widely vary in contaminants and cost in different locations around the world. When considering environmental factors such as water conservation, wastewater reduction and when including infrastructure and labor costs in the evaluation, the analysis of the project can become complex and time consuming.

GE's boiler water solutions bundle chemicals, consumables, equipment and value-added services in a single, affordable package. The program includes some of the industry's best-known and most trusted boiler water treatment technologies. One of the most common causes of forced boiler system outages is boiler tube failure (BTF). Tube metal overheating from gradual accumulation of deposits, or corrosion-induced perforation of tubing from ingress of contaminants, can usually be traced back to water chemistry upsets. In other words, what goes into a boiler system that cannot be "managed" by the water treatment program and subsequently removed by proper circulation and blowdown, will eventually accumulate. The buildup of these materials results in degraded heat transfer and corrosion performance. While variability may exist in the "forgiveness" of a particular boiler design or boiler water treatment, even a well-designed boiler system can be overwhelmed by disregard for the impact of contaminant species on deposition and corrosion processes.



Find a contact near you by visiting www.ge.com/water and clicking on "Contact Us".

* Trademark of General Electric Company; may be registered in one or more countries.

©2009, General Electric Company. All rights reserved.

The purest steam comes from the demineralizer-quality water in the waste heat steam generators. The supply of boiler feedwater can be treated by demineralizers, reverse osmosis units, polishers, electro dialysis reversal, or any combination of these treatments. In high purity boiler feedwater, iron oxides are the main contaminants. The iron is introduced into the system from preboiler heaters and the condensate system. The best way to handle the iron is to prevent it from entering the boilers. However, even small amounts of iron invariably enter the boiler and must be treated. GE conducted several field studies to determine the most effective way to minimize iron contamination and handle the problems it can cause in steam generating systems. Because most high-pressure steam generators have high heat fluxes and use coordinated pH/phosphate programs, iron deposits can cause failures. Concentration of caustic under these deposits leads to caustic gouging and rupture of the tube.

In this report, case history where relevant will be presented that detail the types of failures that can occur as a consequence of exceeding prescribed contaminant limits. The most frequent result, heavy deposit accumulation, can lead to establishment of an insulating layer, reducing heat transfer. Later we will discuss implementing RO treatment of boiler feed water. Internal chemical treatment approach will also be discussed. We will also throw light on GE's new TOC analyzer for boiler water treatment.

Contaminants of Boiler Feedwater

Many of the localized corrosion and embrittlement mechanisms that will be discussed below are operative in steam systems when moisture is carried over, or contaminants are volatilized in the steam phase (i.e., silica and copper at high pressures). Overheating from deposit build-up or blockage of steam flow, under-deposit corrosion (usually from caustic salt carryover), pitting, corrosion fatigue cracking, and embrittlement (mainly caustic SCC) are some of the failure mechanisms encountered in steam path equipment.

Maintenance of steam purity is essential to avoid forced outages in steam system components related to catastrophic fracture or localized corrosion penetration. Carryover of moisture into the steam phase due to water chemistry upsets that induce foaming, damaged or missing steam separation equipment or excessively high steam drum water levels, and/or contamination of the water used for steam attemperation, will eventually accumulate aggressive species in superheaters, reheat tubing, steam, and turbine equipment. Downstream components such as steam expansion joints, condensers, and feedwater heaters exposed to contaminated steam can also fail by SCC or other localized corrosion damage. In particular, stainless steel expansion joints are especially susceptible to caustic SCC in steam systems.¹⁰ Failures can occur rapidly, sometimes within 24 hours of the initial contamination event. In addition, the ingress of ammonia into the steam phase can be significantly detrimental to copper alloy condensers and feedwater heaters. SCC is of primary concern in this case as well. The brass tubing used in these systems is susceptible to cracking in environments containing ammoniacal species.

These failure mechanisms, whether related to gradual degradation or sudden excursions, underscores the need to be ever vigilant in monitoring for upsets and emphasizing proper control in boiler water chemistry and steam purity. The feedwater quality task group of the industrial subcommittee of the ASME Research and Technology Committee on Water and Steam in Thermal Power Systems has published Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers. Many refer to these practices as the ASME guidelines.

The recommended feedwater quality for boiler systems in the pressure range of concern is shown in Table 1.

Table 1¹ - ASME Feedwater Consensus Guidelines for 1501 to 2000 psig (104 to 140 bar) systems

BOILER FEEDWATER PARA-METER ASME CONSENSUS	ASME CONSENSUS
Dissolved oxygen ppm (mg/l), as O ₂ , measured at point prior to addition of oxygen scavenger	< 0.007
Total iron ppm (mg/l), as Fe	<0.010
Total copper ppm (mg/l), as Cu	<0.010
Total hardness ppm (mg/l), as CaCO ₃	ND [not detectable]
pH @ 25oC	8.8 – 9.6
Chemical for preboiler system protection	Use only volatile alkaline materials upstream of attemperation water source

Boiler Tube Failure Mechanism

Frequently, corrosion beneath deposits causes tube failure before sufficient deposit accumulates for over-heating failure to occur. Porous iron oxide deposits usually promote corrosion. Caustic gouging can be found when localized boiling occurs beneath porous sludge deposit on the boiler tube. The mechanism is simple, the water under the sludge turns steam and boiler water is drawn in to replace it. This water contains salts including caustic, the boiling continues and the caustic concentrates very rapidly. Caustic levels of 100,000ppm beneath the sludge are not unknown. High levels of caustic dissolve the protective metal oxide layer on the surface of the boiler tube. The oxide re-forms but is immediately dissolved again. The result is a distinctive gouged pattern of metal removal, which eventually leads to failure. Figure 1 depicts caustic gouging mechanism.

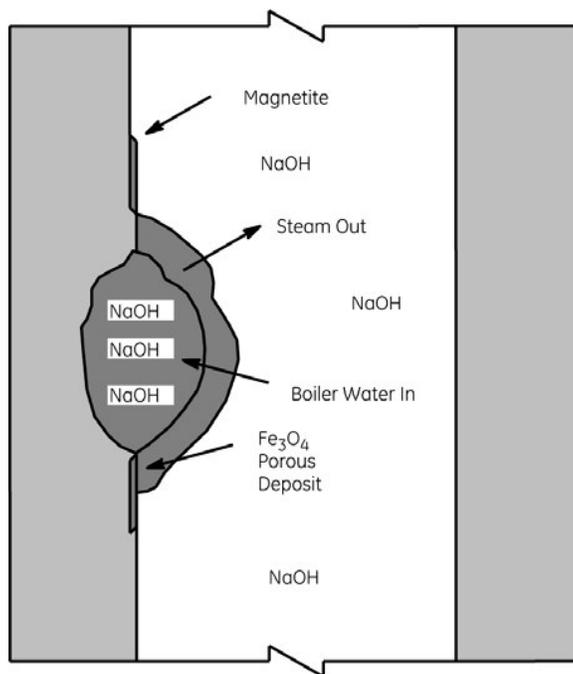
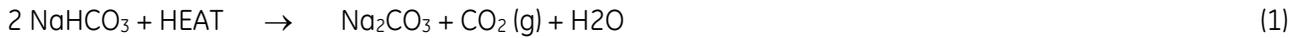


Figure 1 - Porous deposits provide conditions that promote high concentrations of boiler water solids, such as sodium hydroxide (NaOH).

¹ As a general rule, the requirements for attemperation spray water quality are the same as those for steam purity. In some cases boiler feed-water is suitable. In all cases the spray water should be obtained from a source that is free of deposit forming and corrosive chemicals such as sodium hydroxide, sodium sulfite, sodium phosphate, iron, and copper. The suggested limits for spray water quality are: <30 ppb (ug/l) TDS, < 10 ppb (ug/l) Na, <20 ppb (ug/l) SiO₂, and it should be essentially oxygen free.

Dissolved carbon dioxide (CO₂) is the most common cause of this corrosion. CO₂ is produced in the boiler as a result of thermal breakdown of the natural alkalinity, principally bicarbonate ions, which enter with the feedwater. The reactions are as follows:



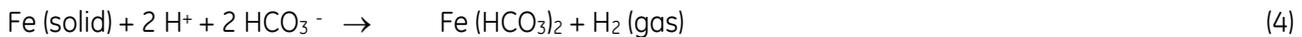
The conversion of bicarbonate alkalinity to gaseous carbon dioxide (reaction 1) is a function of boiler temperature, pressure and residence time. Because it is extremely volatile, the carbon dioxide exits in the boiler with the steam produced. At points of condensation, some fraction of the carbon dioxide present in the steam dissolves in the condensate, forming carbonic acid that hydrolyzes producing hydrogen ions: At points of condensation, some fraction of the carbon dioxide present in the steam dissolves in the condensate, forming carbonic acid that hydrolyzes producing hydrogen ions:



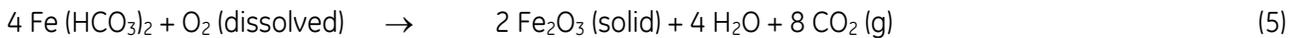
This form of corrosion is controlled by the addition of neutralizing and/or filming amines. Left unchecked, low pH attack in steam condensate driven by carbonic acid takes the form of generalized corrosion, typically forming at bends (where turbulence hastens flow-assisted corrosion (FAC) or impingement), or along longitudinal tracks in horizontal runs.

The hydrogen ions cause acidic corrosion of both iron and copper alloy surfaces in the steam condensate system.

The simplified corrosion reaction for iron is shown below:



The Fe (HCO₃)₂ formed by this redox reaction is relatively soluble, dissociated and its formation is competing with the formation of insoluble iron II oxides such as Fe(OH)₂ or colloidal associations such as Fe (OH)_nⁿ⁻². Additionally, dissolved oxygen is another major cause of condensate system corrosion. Oxygen contamination of steam condensate can occur due to inefficient or improper feedwater deaeration, air leakage at pump seals, receivers and flanges, leaking heat exchangers, and ingress into systems that are under vacuum. In the presence of oxygen, in addition to providing another possible cathodic reaction (1) to pair with the iron oxidation, one more oxidative step is possible 2:



This reaction releases carbon dioxide, which makes the process self-perpetuating. Dissolved oxygen can promote pitting (Figure 2) corrosion that can cause rapid failure of critical equipment in the steam distribution and steam condensate system. Excessive corrosion of the condensate system can lead not only to costly equipment failure and increased maintenance costs, but can also cause deposition of metal oxide corrosion products on boiler heat transfer surfaces if the condensate is recovered as feedwater. Metal oxide deposition on boiler heat transfer surfaces will result in lower fuel to steam efficiency and higher fuel costs. The deposition may lead to tube failure due to long-term overheating.

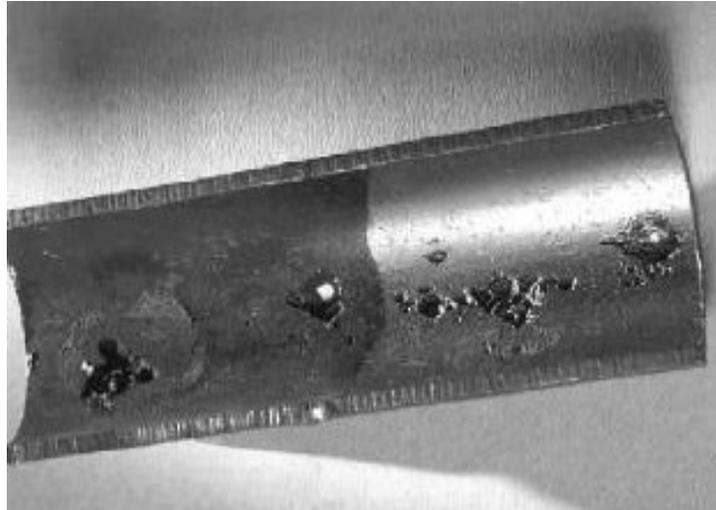


Figure 2 - Oxygen pitting in a boiler tube

Below we present a case study that both corrosion and deposition issues have occurred due demineralizer upset, which in turn led to boiler feedwater contamination.

Case Study – Screen Wall Tubes Failure

Screen wall tubes in a 650 psig boiler were identified to have blistered and leaked in a zone of the boiler that was thought to be subject to flame impingement. However, these failures were not only from flame impingement problems, as inspection of the internal surfaces confirmed white and red deposits that exceeded 200 g/ft².

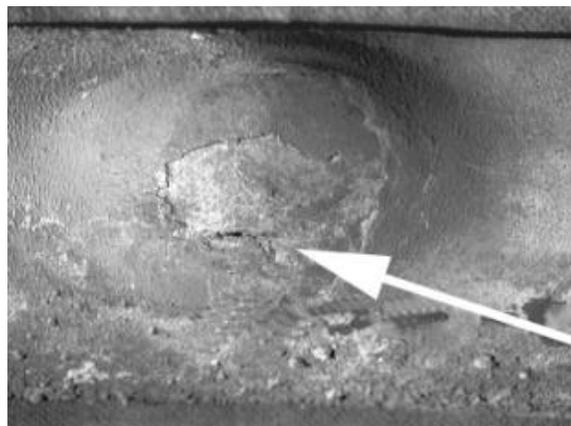


Figure 3 - Creep Blister Rupture, External View

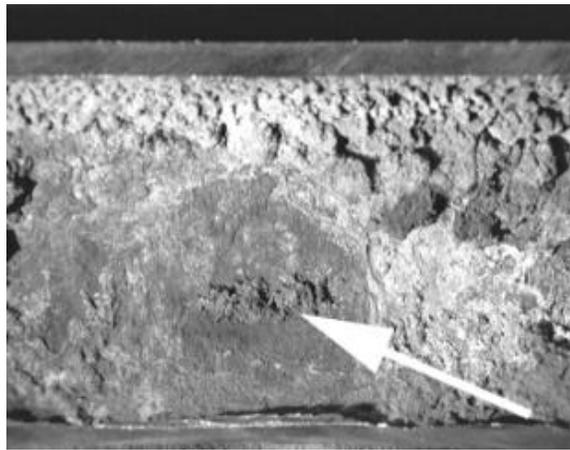


Figure 4 - Waterside Deposit Build-up, around Failure

Review of the operating conditions in the boiler feedwater confirmed demineralizer upsets (hardness and silica excursions), and indicated that the purity of the steam condensate being returned was of variable quality. For example, one condensate stream was documented to have hardness in excess of 2 ppm (from cooling water intrusion), and dissolved copper as high as 0.5 ppm.

Organic contamination of the condensate was also suspected from the occasional “backup” of an adjacent sewage discharge into a steam condensate storage tank. Deposit analysis via scanning electron microscope – energy dispersive X-ray analysis (SEM-EDXA) testing was consistent with the background information, with a composition of 99% copper detected in the top layer of deposit, 35% silica present just beneath the copper-rich material, and hardness salts, copper and iron oxide present in the bulk of the deposit formation. SEM-EDXA mapping showed these deposit layers in a cross-section that had been prepared for metallographic study.

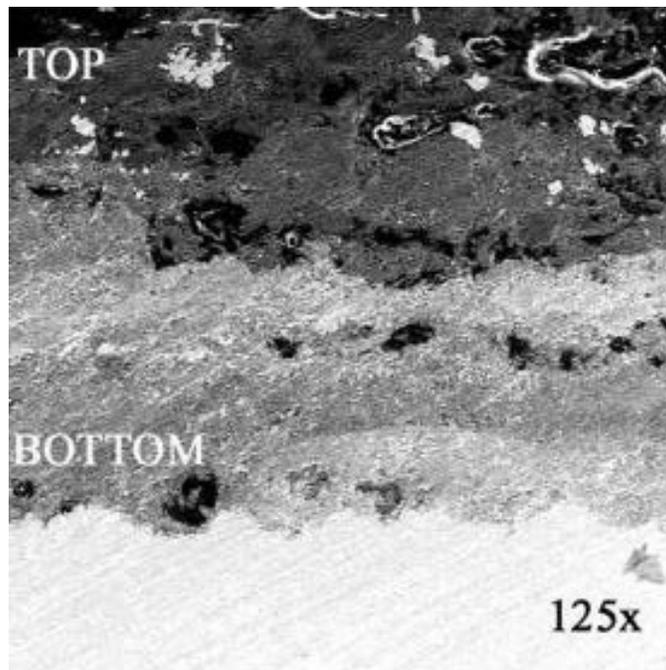


Figure 5 - SEM View of Deposit Cross Section

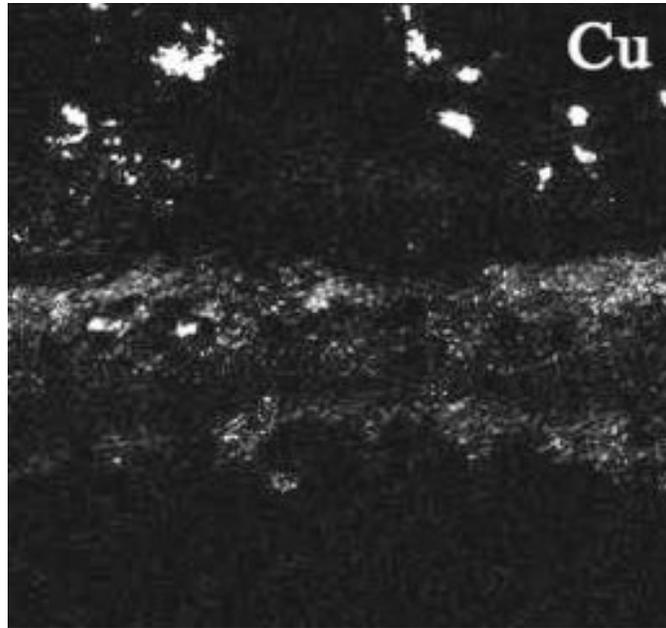


Figure 6 - SEM-EDXA Map of Cu Concentration

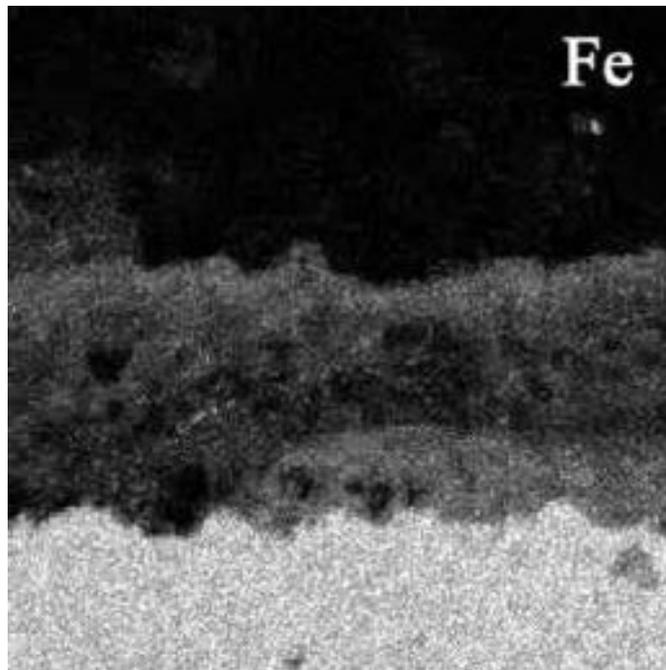


Figure 7 - SEM-EDXA Map of Fe Concentration

Interpretation of the layers in the deposit indicated the probable sequence of events: continuous hardness and iron intrusion, followed by a significant silicon excursion, with a history of copper transport from the condensate return stream that became most intense just prior to the tube blistering problem. Corrective action in this case mandated chemical cleaning of the boiler after appropriate tube replacements, correction of feedwater and condensate contamination problems, and improvement of feedwater and condensate monitoring.

Control Of Feedwater Contaminants And Internal Chemical Treatments To Control Corrosion/Deposition

Feedwater Oxygen Control

To assure operation under a reducing environment, volatile oxygen scavengers are added to the deaerated boiler feedwater. Commonly used chemical scavengers include carbohydrazide, hydrazine, and hydroquinone. Both carbohydrazide and hydroquinone based scavengers were developed to be a replacement for hydrazine, as it has suspected carcinogenic properties. Since a detailed treatise of volatile oxygen scavenging is beyond the scope of this paper, let's leave it that small excess of scavenger assures a reducing environment for the formation of protective magnetite on the surfaces of the boiler and steam systems. High purity feedwater in all steel systems without dissolved oxygen present is passive and protective at elevated pH levels of 9.0 to 9.6. Minimizing the amount of feedwater iron entering the steam drum is a key component of successful internal boiler water treatment. Even a very small amount of transported iron oxide over time can cause problems in boiler systems.

Prevention of Corrosion Failures

A large number of boiler waterside corrosion problems are caused by the concentration of boiler water within or beneath deposits. Therefore, the steps taken to control boiler deposition help to reduce the potential for corrosion. However, corrosion also occurs in areas of steam blanketing and where the metal is highly stressed, such as at weld attachments. Consequently, to control corrosion problems, it is necessary to maintain the boiler water chemistry so the contaminants and the additives in the boiler water do not become corrosive, even when they are concentrated. This can be accomplished by maintaining extremely pure feedwater so that potentially corrosive contaminants do not enter the feedwater circuit. To do this, mixed bed demineralized makeup water and polished condensate are usually required. Plants that consistently maintain very high purity feedwater can protect their system from corrosion by using only volatile treatment chemicals, an oxygen scavenger, and an amine for pH control. This all-volatile treatment (AVT) is used successfully in a small number of industrial boilers in the United States. However, even with sophisticated water treating equipment, plants often encounter operating problems that cause feedwater contamination. As a consequence, it has become common practice to apply phosphate to control the boiler water chemistry. The use of phosphate prevents low levels of feedwater contaminants from causing damaging pH excursions.

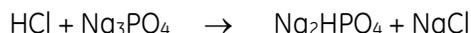
Most high-pressure industrial boilers with high purity feedwater use a phosphate-based chemical treatment program for corrosion control. The evolution of phosphate-based boiler chemistries followed improvements in feedwater quality. Prior to the advent of demineralizers, sodium phosphates were used to precipitate calcium to a calcium hydroxyapatite that was a fluid sludge removable by lower drum blowdown. When demineralized water systems came about, the need for hardness precipitation was replaced by a need for phosphate buffering. The buffering action of the phosphate treatment will minimize the potential for acid and caustic based corrosion. Keeping a clean heat transfer surface is key to minimizing under-deposit corrosion cells. Deposit minimization relies on both the feedwater treatment and polymeric dispersants. Besides causing boiler tube overheat failures, deposits play a role in corrosion. Formation of concentration cells under and within deposits can lead to corrosive conditions at the tube metal surface. As such, the maintenance of clean boiler tube surfaces is the most important step that one can take to minimize corrosive attack.

Coordinated and Congruent Phosphate

The first use of phosphate chemistry programs 4/5 for corrosion control dates back to the early 1940s when Whirl and Purcell developed coordinated phosphate/pH for control of caustic embrittlement. The basis of the chemistry is:



As shown above, feedwater caustic will react with disodium phosphate in the boiler water forming trisodium phosphate. In a similar fashion feedwater acidic species will react with trisodium phosphate to form disodium phosphate as follows:



By controlling the boiler chemistry to maintain dibasic phosphate in the boiler (sodium to phosphate molar ratio less than 3.0 to 1), caustic (NaOH) cannot concentrate, and cause corrosion. This assures that all the sodium is associated with phosphate and no free NaOH is in solution. By maintaining the alkalinity as a captive phosphate alkalinity, under deposit concentration of caustic is eliminated, thereby minimizing caustic gouging potential. Coordinated phosphate programs were designed to prevent caustic gouging, but such problems persisted even when coordination was maintained. The gouging was associated with boiler deposits and it suggested that the gouging was related to the extent of the deposition. It was also noted that phosphate precipitation occurred at a lower ratio than the 3.0 originally prescribed for coordinated control.

These observations made researchers re-think the sodium phosphate buffer chemistry under the boiler environments where problems were observed. As a result of further studies of solution chemistry and two-phase equilibrium, a new definition of phosphate control was developed around solubility data. Research data showed that pure sodium phosphate solutions at 572°F (300°C) form precipitates at a 2.85 to 1 sodium-to-phosphate ratio. This led researchers to propose an upper limit for maintaining sodium-to-phosphate congruency. Further definition of the chemistry⁹ found two invariant points, one at 2.85:1 and one at 2.15:1. These boundaries became the upper and lower limits for the congruent control utilized by most industrial boiler systems today. Even though congruent control can maintain pH during minor contaminant ingress and to a minor extent inhibit calcium deposition during hardness intrusion, its primary purpose is to mitigate underdeposit corrosion. It performs this task by maintaining under-deposit sodium phosphate solution chemistry between the congruency limits. By doing this, the concentrated solution under a boiler deposit does not result in either caustic gouging or acidic phosphate corrosion.

Figure 8 shows the relative corrosion of carbon steel boiler tubing operating at 590°F (310°C) as a function of pH and concentration of corroding species – HCl and NaOH.

For years congruent phosphate programs have been applied with the assistance of a logarithmic control chart as that shown in Figure 9.

Several upper molar ratio boundaries are presented depending on the operating pressure of the boiler. These boundaries were set to assure minimal chance of phosphate precipitation at the corresponding temperatures. Staying below the upper molar ratio limit will minimize the chance of caustic concentration and gouging of the tube metal. The lower control boundary of 2.2: 1 molar ratio is set to minimize the chance of acidic phosphate attack. When the boiler pH and phosphate levels stay within the control boundaries, the boiler water should be non-corrosive. The vector diagram indicates the direction a point will go on the phosphate-pH diagram if a certain chemical is added to the system. Also shown is the affect of increased continuous blowdown.

In thinking of powdered sodium phosphates, one can imagine the need for three phosphates as well as caustic. When dealing strictly with powders, this could be the case, but normally only tri and disodium phosphate will be required to counter normal contaminant variation in the incoming boiler feedwater. Most water treatment companies can provide blends of sodium phosphate products at various sodium to phosphate molar ratios.

Staying within the control boundaries of phosphate and pH is key to successful operation of high-pressure industrial boilers. But both of the corrosion pathways are connected with deposits.

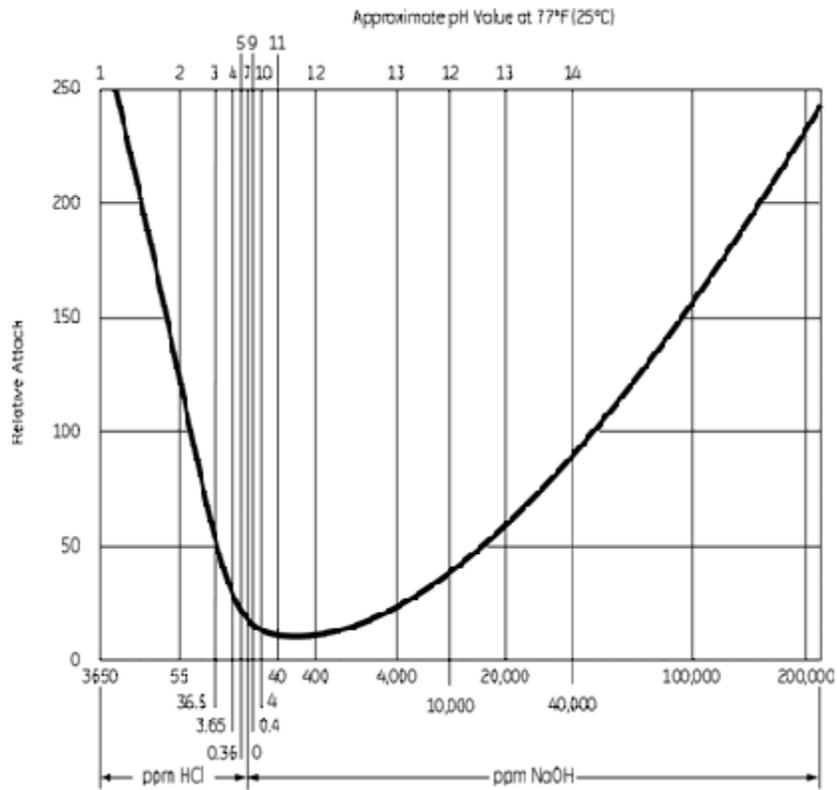


Figure 8 - Relative corrosion of carbon steel by HCl and NaOH at 590°F (310°C). (Berl and vanTaack, 1930; Partridge and Hall 1939)

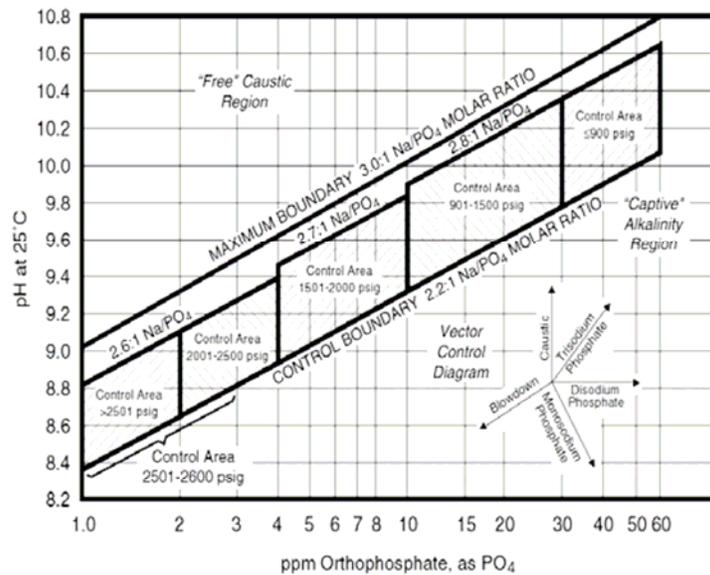


Figure 9 - Coordinated Phosphate/pH Control Chart

Prevention of Overheating Failures – Dispersants

Usually, overheating failures are caused by deposit accumulations on the tube surfaces. If not treated with an effective boiler water dispersant, virtually all feedwater iron, copper, calcium and magnesium remains within the boiler. These feedwater contaminants deposit on the boiler metal surfaces, accumulating primarily in areas of low velocity or high heat flux. The deposits restrict the transfer of heat from the furnace gases to the boiler water causing the tube metal temperature to increase. Deposits in high heat flux areas are the most damaging as they cause the highest metal temperature increases. If excessive deposits accumulate, the tube metal temperature becomes so high that creep failure occurs.

Historically, dispersants for low pressure boilers (below 900 psig) have been used to control hardness scale and, to a lesser degree, iron scale. High-pressure industrial steam generating systems (900-1700 psig) use dispersants primarily for iron deposition control. However, in some high-pressure systems, significant iron deposits form despite the presence of polymer. One reason for failure may be underfeed of polymer. Another reason may be the loss of polymer activity due to hydrothermal decomposition at high temperatures and/or extended residence times.

To overcome the efficiency loss in high-pressure systems, GE Water & Process Technologies has invented a new polymeric dispersant. It is an organic molecule designed specifically for iron deposit control in higher-pressure steam generating systems. This new polymer is known commercially as HTP-2 dispersant.

Laboratory research boiler studies were performed at 1450 psig under congruent phosphate control. Feedwater contaminated with iron was used. Polymer dose/response curves were constructed for: polyacrylic acid [PAA], polymethacrylic acid [PMA], copoly (acrylic acid/acrylamide) [PAAM], and HTP-2. In research boiler studies, where PMA showed 65% deposit inhibition, PAA showed 70% inhibition, PAAM showed 40% inhibition, while HTP-2 showed 89% inhibition. As the polymer concentration increased, PMA and HTP-2 showed continued polymer performance, while the acrylate-based polymers showed inconsistent activity. Boiler blowdown iron concentrations were comparable for all polymers except HTP-2, which showed superior transport activity.

Figure 10 shows the relative iron pickup of PAA, PMA, PAAM, and HTP-2 across the research economizer. PAA and PAAM show the highest iron transport of the four polymers, with PAAM being the highest. The new polymer, HTP-2, was virtually indistinguishable from PMA. Figure 10 shows that HTP-2 is less corrosive towards iron based metallurgy than PAA or PAAM and equivalent to PMA.

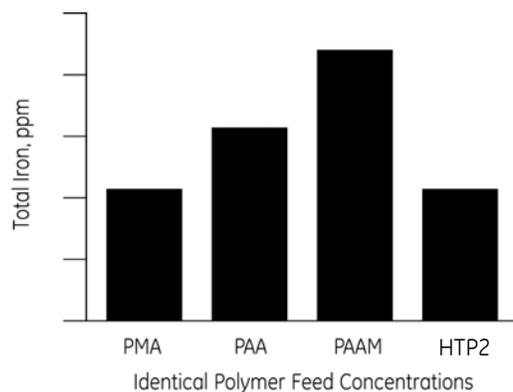


Figure 10 - Research Economizer: Relative Iron Transport

Four field trials are presented here: a 1500-psig ammonia boiler, a 1250-psig paper mill combination boiler, a 1500-psig chemical plant boiler, and a 1500-psig utility boiler. In all four field trials, HTP-2 was introduced directly to the steam drum. Whenever possible, samples were taken prior, during, and after introduction of the new polymer to monitor effects of the new additive.

Total iron, orthophosphate, and pH were measured on blowdown samples to determine changes in iron transport and to determine if there were any effects on congruent control. Graphical profiles of the trial data are presented. They show the changing iron transport during the polymer application while proper congruent control was maintained. In one trial, the boiler blowdown iron concentrations increased from < 25 ppb to near 800 ppb after introduction of the polymer. In another the blowdown concentration increased from < 50 ppb to 300 ppb. In a third the change was from < 1 ppm to 16 ppm, while in the fourth the change was from < 10 ppb to 150 ppb.

Improve Feedwater Chemistry with RO

The addition of a reverse osmosis (RO) system to a boiler plant, which originally only had sodium zeolite softening of the make up water significantly, improves the purity of the boiler feedwater. The lower dissolved solids water produced by the RO and greater consistency of treatment reduces the potential for boiler and steam system deposition and corrosion enabling our customers to reduce boiler blowdown, saving both energy and water treatment chemicals. In addition, because the alkalinity of the RO treated water is lowered carbon dioxide in the condensate is reduced and the potential for condensate system corrosion lowered.

The many potential benefits that can be derived by adding an RO to a softened water system can be fully realized only with a water chemistry program that takes into consideration the revised water characteristics and the operating requirements of the plant. Adding an RO system to plants with high sodium or silica leakage from the demineralizer plant can also significantly improve steam purity. This is most pronounced in plants that inject boiler feedwater for steam attemperation or desuperheating. This is a common and sometimes overlooked source of steam contamination.

Overall, implementing RO treatment of boiler makeup water can substantially improve steam purity and often eliminate steam system fouling and corrosion problems as can be seen from the case study below.

Case Study – RO for Boiler Feedwater Makeup Treatment

A United States Midwest oil refinery provided their boilers with boiler feedwater consisting of 50% to 75% hot lime-hot zeolite softened makeup water and 25% to 50% condensate return. The boilers produce steam at 600, 450, 220 and 125 psig. The maximum boiler blowdown water conductivity limits in this refinery are 3000 $\mu\text{S}/\text{cm}$ for the 600 psig boilers and 5000 $\mu\text{S}/\text{cm}$ for the 450 psig and lower pressure boilers. Blowdown from the boilers goes to 50 psig flash tanks that vent steam to the refinery's low-pressure header and discharge the liquid to waste.

Raw water is obtained from a canal that is subject to contamination from run-off of adjacent roadways. Conductivity of the canal water, which is normally about 1000 $\mu\text{S}/\text{cm}$, increases to 2000 $\mu\text{S}/\text{cm}$ due to salt contamination from the run-off in the winter months. During these times, it was impossible to blow down the boilers enough to keep boiler water conductivity within the specified limits. Despite feeding boiler water anti-foam, unacceptable levels of boiler water carryover occurred during these episodes.

Steam turbine fouling occurred from chronic boiler water carryover and turbine washes were required every few weeks. Additionally, the blowdown flash drums were ineffective for separating the water from the steam at the high boiler blowdown rates necessary when the high conductivity boiler makeup water was being used. Consequently, boiler blowdown water carried over from the flash tanks into the low-pressure steam line creating the need for routine condensate flushing of this line to remove deposits.

In one instance, when operating a package boiler with the continuous blowdown valve wide open did not maintain the boiler water conductivity within range, the manual blowdown valve was left open to help reduce the boiler water conductivity. Operating with the manual blowdown valve continuously open reduced the water circulation in the generating tubes near the manual blowdown take-off, which caused the tubes to overheat, form blisters and rupture.

Installing an RO system to treat some of the softened makeup water proved successful. The RO permeate conductivity typically ranges from 15 to 30 $\mu\text{S}/\text{cm}$, a dramatic improvement compared to the softened water. Boiler blowdown rates have been reduced so they now vary from 2% to 10% of the boiler feedwater depending on the quantity of softened water that by-passes the RO system.

Energy savings from the lower blowdown rates are estimated to be over 250,000 million BTUs per year. Additionally, reducing (and soon eliminating) the need for turbine and condensate line washings increases plant reliability and improves safety. Due to these benefits, the refinery is evaluating the use of additional RO equipment to treat all of their boiler makeup water during future winters to further improve their steam plant performance.

Improved Condensate System Corrosion Control

Effective condensate system corrosion control enables reliable, energy efficient plant operation. Condensate system corrosion causes equipment and piping failures. Costs increase as plant equipment and piping must be replaced more frequently. Often more costly are the losses of plant production and the ability to return valuable, high energy, high purity condensate to the boilers. Poor condensate corrosion control increases the quantity of iron and copper corrosion products returned to the boiler feedwater with the condensate. Boiler deposits formed by these corrosion products increase the potential for boiler tube failures. In plants where the feedwater is used for steam attemperation or desuperheating, corrosion products in the feedwater may form deposits in control valves and on turbine blades and cause solid particle erosion of turbine blades.

GE has a complete line of condensate system corrosion inhibitors, encompassing acid neutralizers (Steamate* NA), film formers (Steamate FM and Steamate NF) and metal passivators (Steamate PAS). In addition GE's unique proprietary condensate modeling ability (CMS) enables us to identify the best products, feed points and feedrates for complex steam-condensate systems. Effective, economical treatment of condensate systems with high carbon dioxide content cannot always be achieved with chemicals alone. In these instances, the addition of RO equipment to remove alkalinity from the makeup water significantly reduces the potential for condensate system corrosion. Lower alkalinity in the makeup water translates into lower carbon dioxide in the steam, the main contributor to most condensate system corrosion.

Condensate Modeling System for Optimal Corrosion Control

GE Water & Process Technologies has also developed a unique Condensate Modeling System (CMS) for optimal corrosion control. This tool assists in the formulation, application, optimization, and troubleshooting of boiler and condensate treatment programs. CMS is a significant advancement in boiler and condensate treatment performance optimization and control. It can be applied to optimize both condensate and boiler chemistry. The CMS simulation program goes beyond conventional methods of boiler and condensate modeling and treatment optimization by using:

- State-of-the-art computer graphical interface
- Equation solver technique
- Sophisticated methods for calculating chemical distribution

As a result, CMS is capable of ensuring timely optimization for even the most complicated systems. When using only the conventional method of chemical treatment selection and application, the system can frequently be out of control. Operations personnel monitor the condensate system for pH, iron, copper, etc., then adjust the amine feedrate until system control is regained. However, your GE representative can help

provide a more reliable treatment program control using detailed knowledge of your system and CMS. Optimal, cost-effective treatment and an increase in troubleshooting productivity are achieved.

Tools To Evaluate Boiler Treatment Equipment Options

To address the issue of the production of clean boiler feedwater, GE has developed a range of tools that allow for a quick but thorough evaluation of key factors for both new projects as well as system upgrades. These tools allow evaluation of Pretreatment options, Softening, Ion Exchange (IX), Ultrafiltration (UF), Reverse Osmosis (RO), Electrodialysis Reversal (EDR), Electrodeionization (EDI) and Thermal Evaporation and various combinations thereof. The tools are designed to be used in the planning stage of a new project or system upgrade. Starting with a range of key inputs and assumptions they provide detailed information on capital and operational costs. A payback time is calculated for a system upgrade with limited input data being required. For new systems the tools provide a comprehensive comparison of alternative system designs, without the need for a detailed design of each option. Early in the process it will become clear which technologies are most attractive, depending on the feedwater analysis and site-specific factors, including input costs, and operating conditions. The result allows the utility manager or application engineer to come to a comprehensive and definitive conclusion in a matter of hours.

The tools that we have developed include:

1. Addition of a RO unit to an existing Softener, to feed a low- or medium-pressure boiler.
2. Addition of a RO unit in front of an existing conventional Demin system using Ion Exchange technology, to feed a medium- or high-pressure boiler.
3. UF plus RO to replace an existing Hot Lime Softener, to feed a medium- or high-pressure boiler.
4. RO plus EDI versus Ion Exchange, to produce high purity water to feed a high-pressure boiler.

Online Monitoring Of Boiler Feedwater

A boiler system consists of several key components susceptible to corrosion. If corrosion occurs in any of those components, it leads to boiler inefficiency. In addition to pH & Conductivity, one leading measurement to indicate corrosion is the presence of organics. By monitoring total organic carbon (TOC) in the boiler water, the system integrity can be monitored and corrected before any detrimental consequences occur. Most plants set maximum limits for TOC in boiler feedwater with the level depending on the pressure of the boiler. Typically, the lower the pressure, the lower the purity requirements. Ion exchange or physical processes like ultrafiltration can remove the majority of organic compounds found naturally in water. Some organic compounds, however, require additional steps for their removal or destruction.

GE Sievers InnovOx TOC Analyzer

GE Analytical Instruments has made innovative strides in TOC analysis, focused on providing a robust analyzer for the most difficult matrices. GE's TOC Analyzer has taken innovation to a new level. By using an ultra-efficient Supercritical Water Oxidation (SCWO) technique, the InnovOx is able to run hundreds of water samples continuously with no recalibration, no system maintenance, and no replacement parts.

The TOC analyzer principle of operation is based on the wet chemical oxidation technique, which adds an acid and oxidizer to the sample of interest. The inorganic carbon is removed by purging, and the sample is then oxidized with persulfate at elevated temperatures. The resultant carbon dioxide is measured by a non-dispersive infrared spectrometer resulting in superior accuracy and precision measurement of TOC.

By using an ultra-efficient Supercritical Water Oxidation (SCWO) technique, the InnovOx is able to run hundreds of water samples continuously with no recalibration, no system maintenance, and no replacement parts. Using an oxidation process in a super critical state has shown superior TOC recoveries across a broad range of organic compounds and particulate impurities. This new process removes sample and precipitated

impurities between each analytical run, eliminating sample matrices contamination and providing reliable, long-term system performance.

Controlling TOC in power applications is critical to protecting turbines, steam generators, and condensers from the corrosive effects of organic acids.

GE Analytical Instruments manufactures the only TOC instruments with ASTM-approved methods for both on-line (Method D 5997) and laboratory TOC analysis (Method D 5904).



Figure 11 - GE's Sievers 900 On-Line Total Organic Carbon (TOC) Analyzer

The figure below shows the monitoring of water over an extended time period. The TOC level remains well under the required minimum concentration specification set by the plant manager. In this scenario, the limit is set at 80 ppm TOC. If TOC exceeds a critical level, the operator quickly reports the event and corrects the situation.

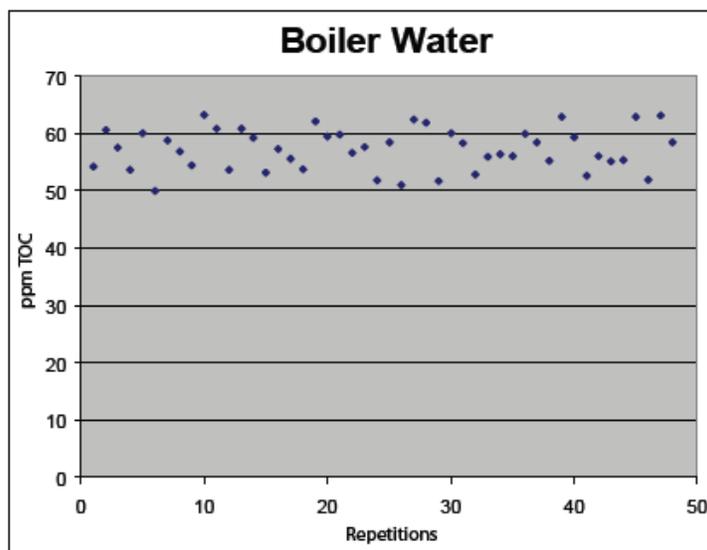


Figure 12 - TOC Recoveries in Boiler Water

Conclusion

Selecting a treatment program appropriate for the system operating conditions will reduce the frequency of industrial boiler tube failures. Through this review, we share the spectrum of GE's technologies to address some of the critical issues faced in boiler operations. To put together an effective treatment strategy it requires thorough evaluation of the situation first (typically through a system audit) and then putting together a coordinated strategy of water treatment (RO), chemistry management and monitoring to affect a trouble free operation.

References

1. Esmacher Mel J., "The Impact of Water Chemistry on Boiler Tube Failures" presented at the 25th annual electrical utility chemistry workshop at the university of Illinois, USA, May 2005.
2. Rosa Crovetto, Eunice Murtagh "Novel Boiler Condensate Corrosion Inhibitor with FDA Approval", 2007 NACE Corrosion Conference & Expo.
3. Paul Cohen, Ed., "The ASME Handbook on Water Technology for Thermal Power Systems", The American Society of Mechanical Engineers, 1989.
4. Paul Tan, "Optimizing a High-purity Water System", Tall Oaks Publishing Inc., 2007
5. Beardsley, S., Coker, S., and Whipple, S., "The Economics of Reverse Osmosis and Ion Exchange", Paper presented at WATERTECH '94, Nov 9-11, 1994.
6. Henley, M., "Treatment Polymers for Corrosion and Scale Control", Industrial Water Treatment, 24 (3), pp. 17-26 (1992)