

SOME COMMON MECHANISMS LEADING TO FAILURES IN HEAT RECOVERY STEAM GENERATORS

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ABSTRACT

Failures due to flow accelerated corrosion have occurred in the economizers and the low pressure generating sections of a number of HRSG's. Deposit accumulation in the high pressure generating section has presented difficulties in many of the same units. Three case histories are presented illustrating the conditions, which have lead to component failures in some Heat Recovery Steam Generator systems.

Keywords: Flow Accelerated Corrosion, Corrosion, Failures, Heat Recovery Steam Generators (HRSG's).

INTRODUCTION

Large numbers of combined cycle systems (Gas Turbine Units coupled with Heat Recovery Steam Generators) have been put into service to generate power in the United States over the past 20 years. This is because they offer a very efficient means of power generation and they can be built relatively quickly and inexpensively compared to conventional fossil fired generating systems.

Combined Cycle Systems

Gas turbine sizes vary from 1 MW to over 200 MW. Heat Recovery Steam Generator (HRSG) designs vary from simple single pressure systems to more complex multiple pressure designs. Water

treatment approaches are varied to accommodate the multiplicity of designs and operating pressures in use in systems today. Most systems operate with demineralized make up water combined with relatively high quality condensate for boiler feedwater. Drum units, which operate at two or more pressures pose special challenges in the selection of water treatment chemistry. Optimum treatment chemistry may be different for individual pressure stages. In many cases HRSG's are designed with the low pressure circuit functioning only to provide steam for the deaerator. In other cases cascading blowdown is utilized where blowdown from the HRSG high pressure circuit may be directed to the intermediate pressure or low pressure circuit increasing the conductivity in these circuits and often complicating control of the chemical program.

Many combustion turbine/HRSG combined cycle systems are installed in manufacturing facilities to provide steam and power for the facility together with power generation for the grid. The condensate returned from the plant process is subject to contamination, which can be quite severe. In these cases adequate provisions for condensate polishing are essential to ensure the supply of boiler feedwater of appropriate purity to the system.

Many combustion turbines require significant quantities of water or steam to reduce NO_x emissions and /or to increase power output from the combustion turbine system. The water or steam utilized must be of sufficient purity to avoid deposition or corrosion in the unit.

With appropriate feedwater, the water treatment program is designed to maintain clean corrosion free waterside surfaces in all areas of the HRSG. However in many cases the design or mode of operation of the unit increases its susceptibility to waterside damage.

Flow Accelerated Corrosion in HRSG Units

Flow accelerated corrosion has been observed in economizers and in the low pressure steam generating sections of a number of HRSGs.

HRSG Tube and Header Metal Loss in the Low Pressure Generating Section.

The thinning of the first few rows of tubes in the low pressure generating section due to a flow accelerated corrosion mechanism has been identified in a number of HRSG's. This would appear to result from a boiler design issue in that the fluid flow rate in those tubes appears to be high enough to contribute to accelerated corrosion at the tube surface in the upper area of the tube with the metallurgy originally installed.

The primary issue appears to revolve around the rate of steam generation in the first few rows of tubes in the low pressure generating section in the affected units. The velocity increases rapidly as the fluid (steam/water mixture) rises up the tube, due to the volume occupied by the steam at low pressure. For example at 15 psig (0.1034 MPa) one pound (0.4536 kg) of steam occupies 13.7 cubic feet (0.388 m³) while one pound of water occupies 0.016 cubic feet (0.000453 m³). If 10 % of the water passing through the tubes in a 15 psig (0.1034 Mpa) circuit is converted to steam the volume of 100 pounds (45.36 kg) of the fluid will increase from 1.67 cubic feet (0.0473 m³) to 138.44 cubic feet (3.921 m³) an increase of almost 8300%. So the steam generated in the tube produces a large increase in fluid volume and hence fluid velocity as the fluid rises up the tube.

Changing the metallurgy in the affected tubes appears to have eliminated the metal loss in the tube walls however in many cases the issues of metal loss in the upper header system and the baffles in the low pressure drum are yet to be fully resolved. The impact of metal loss in the upper header is a far larger problem than in the tubes in that replacement of the header would be a more expensive project

HRSB Metal Loss in Economizer Tubes

In a number of units economizer tubes have been replaced following thinning due to pitting corrosion. Also thinning has been noted in the stubs off the lower headers of economizers possibly due to a flow accelerated corrosion mechanism. The resulting corrosion debris circulating in the water can cause additional metal loss due to erosion as well as deposits in the economizer and the high pressure generating section of the affected unit.

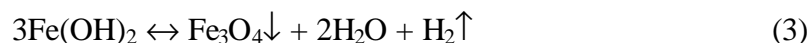
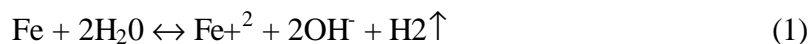
HRSB Deposits in High Pressure Generating Tubes

Deposits have been noted in the tubes at the front end of the high pressure system in a number of units. These observations provide an additional indication of the presence of iron oxide based corrosion product in the high pressure boiler water in the affected units. The deposits in the front of the high pressure generating bank could lead to overheating failures or under deposit corrosion failures in these tubes.

Boiler Internal Surface Passivation

Waterside metal surface passivation in an operating boiler is a slow controlled corrosion process, which takes place on a continuous basis. Under normal operating conditions, internal boiler corrosion leads to the formation of magnetite on the metal surfaces with the release of hydrogen. This process occurs naturally even though operating conditions are designed to minimize corrosion.

The control of corrosion in a boiler environment is based on maintaining conditions, which enhance passive film formation. Magnetite is the preferred high temperature iron oxide form. Well crystallized (unhydrated) magnetite forms a dense layer resulting in excellent passivation. Schikorr^{1,2} established a mechanism for the formation of magnetite as follows:



In this process, it has been shown that the formation of the ferrous hydroxide (Reaction 2) is the rate determining step. Therefore, the solubility and stability of this reaction product is the key to corrosion protection in the boiler³.

Passivation is a process in which the metal surface converts from the actively corroding to a relatively inactive state. Reactions 1-3 illustrate this process relative to magnetite formation. These reactions also show that hydrogen is released as the metal corrodes to form magnetite.

Under good boiler operating conditions hydrogen evolution due to the oxidation of iron to magnetite at the metal surface is slow because the magnetite forms a fine tightly adherent layer with good protective properties. The film generally displays good adhesive strength in part because the thermal coefficients of linear expansion for magnetite and steel are very similar. Therefore, varying heat load and surface temperature do not cause undue stress between the film and the underlying metal surface⁴.

Waterside deposit accumulation can also create an environment where active corrosion of the boiler tube metal surfaces can occur. This is due to the initiation of concentration boiling cells within the deposit leading to over concentration of boiler solids at the tube surface⁵.

Concentration boiling mechanisms can occur within or under the deposit. If the deposit is relatively porous (often the case in deposits containing significant proportions of iron oxide) water will be drawn to the hot surface through the pores by capillary action similar to a fluid permeating a wick. Steam is generated at the surface, which passes out of the deposit via other pores or channels allowing more boiler water to permeate the deposit. Under these circumstances where normal washing of the tube surface is precluded by the deposit a very high concentration of boiler water solids can occur which can often result in rapid corrosion of the metal surface. A number of different corrosion mechanisms can ensue, one commonly found mechanism is caustic corrosion.

Caustic Corrosion

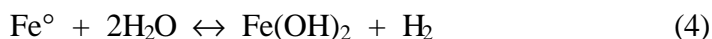
Caustic corrosion is referred to as “caustic attack”, “caustic gouging”, or “ductile gouging”. Corrosion of this type generally results from fouled heat transfer surfaces and the presence of an active corrodent (sodium hydroxide) in the boiler water^{6,7}. Concentrated solutions of alkali occur in situations where the normal washing of the tube metal is restricted after steam bubble release.

Feedwater solids concentrate in the boiler relative to blowdown rates. Boiler water solids may concentrate an additional 2,000 times at the heat transfer surface as a result of a “concentration film” produced from non-boiling equilibrium⁷. The formation of a steam bubble further concentrates boiler solids. These conditions are most likely reached in the presence of a porous scale.

Once local caustic concentrations are reached such that caustic attack occurs, the corrosion can proceed to failure in a very short time⁸. Caustic corrosion results in irregular wall thinning or gouging of the tube’s waterside surface⁹. Areas subjected to caustic attack typically show smooth, rolling contours surrounded by encrusted boiler water solids and crystalline dense oxides. The oxides, however, are not protective. Particles of metallic copper may also be embedded in the scale layer.

Failures due to caustic attack are caused by metal loss. The damage progresses to failure when the tube wall thins to a point where rupture occurs locally. The microstructure does not change and the tube metal retains its ductility⁹.

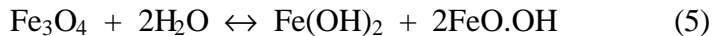
The basic reaction of iron and water under alkaline conditions produces iron hydroxide as shown in the following equation:



The Schikorr mechanism for the formation of magnetite was reviewed earlier in this discussion.

The solubility of magnetite under alkaline conditions is a complex subject; therefore, the following is only a brief discussion of the equilibrium involved³.

Magnetite is considered to be a copolymer of the hydroxides of iron (III) and iron (II). It can also be considered as a homogeneous solid solution of Fe in Fe₂O₃. In this system, the bonds of the divalent iron are more easily hydrolyzed. Therefore, the iron (II) hydroxide system (aqueous) is considered to be in solution equilibrium with magnetite as follows:



Under highly alkaline conditions the ferrous hydroxide in solution may react as follows:



Caustic attack occurs in this manner through activation of the carbon steel surface by removal of the passive oxide layer or inhibiting its formation. These conditions lead to the formation of a velvet-black, finely crystalline, reactive magnetite. It has low adherence and practically no protective effect.

The presence of an iron-based deposit in the boiler often creates the conditions where over concentration of the boiler water in the deposit can result in high concentrations of sodium hydroxide leading to caustic attack.

In HRSG systems deposition is usually in the form of metal oxides. The source of the metal oxides is corrosion of plant equipment, in the steam condensate system and boiler feedwater system. In cases where flow accelerated corrosion is identified significant amounts of suspended magnetite are often found in the water. The corrosion products are transferred into the boiler in the feedwater. The majority of corrosion products consist of colloidal and particulate metal oxides¹⁰. In the condensate system an amorphous or gelatinous solid is usually formed when ferric or ferrous ions initially precipitate.^{11,12,13} The iron hydroxide may deposit at the metal surface as a permeable or impermeable film at the corrosion site when the corrosion rate is very low. At higher corrosion rates, iron ions, hydroxides and oxides are transported into the bulk solution. Iron oxide precipitates formed under these conditions are typically colloidal and form stable suspensions.^{11,12,13} Once formed, iron containing particles age and form a more crystalline material.¹¹ **Table 1** illustrates many of the reactions involved in generating iron oxide corrosion products as a result of condensate system corrosion.

Table 2 lists the physical properties of iron based corrosion products, which may be found in preboiler systems.^{12,13,14,15,16}

Once in the bulk condensate, corrosion products are transported into the preboiler system, carried into the economizer and on into the steam generating section of the boiler, where the iron oxide particulates preferentially deposit on boiling heat transfer surfaces.^{16,17,18}

An additional parameter considered when iron oxides are formed is the electrostatic attraction of the particles.¹⁸ The electrostatic charge of iron oxide particles is pH dependent and based on its isoelectric point. A reported isoelectric point-solid (IEPS) for Fe₂O₃ is 6.7. This number was determined using naturally occurring hematite, washed until free of ions and analyzed utilizing microelectrophoresis.¹⁹ This number is the pH value at which an immersed solid oxide surface has zero net charge and/or the pH value which results in electrically equivalent concentrations of positive and negative complexes. However, the compound Fe₂O₃ (hydrous or amorphous) has an IEPS of 8.7.¹⁹ This number was developed using synthetic Fe₂O₃ generated by hydrolysis and aging at 90°C followed by analysis using microelectrophoresis.¹⁹ Therefore, hydrated iron oxides precipitated from solutions with a pH less than 8.7 typically have a positive surface charge.¹⁹ This may be due to the high affinity for hydrogen ions (H⁺) exhibited by the hydroxyl sites (OH) in the solid phase. This is one reason for the high affinity of iron oxides for anionic species. Conversely, where the precipitation occurs under high pH conditions, hydroxyl ions are the primary adsorbents resulting in a negative surface charge.

A second possible explanation is that iron precipitation in a lower pH environment is hydroxide ion deficient resulting in inefficient shielding of the large positive cation (Fe⁺², Fe⁺³). In high pH waters, the cation (Fe⁺², Fe⁺³) is effectively shielded by the negative charge of the hydroxide groups.¹³ It has been reported that hydrated iron oxides generated under condensate and preboiler system conditions have a positive surface charge¹⁹ and that iron oxides produced under boiler pH conditions have a negative surface charge.^{18,19} Laboratory surface charge measurements for synthetic iron oxide where morpholine, cyclohexylamine and sodium hydroxide were used to adjust pH conditions show no apparent difference, in agreement with the previous observations.²⁰ Field studies also appear to support these observations.^{11,16} The observations on surface charge characteristics are important in that they provide an explanation for the performance of low molecular weight anionic polymers in preventing deposition of iron oxide particulates.

In the boiler unit iron oxides are primarily deposited on heat transfer surfaces developing a porous scale layer. Surface chemistry studies have shown that hydrophobic iron oxide particles are trapped on the water/steam bubble interface during boiling.¹⁷ These particles agglomerate and preferentially concentrate on the metal surface after the bubble is released. Electrostatic and intermolecular forces bind the deposited particles sufficiently to prevent their being reentrained into the bulk solution.^{16,18} Thermal effects fuse the particles to the surface. The scaling particles then take on the same charge characteristics as the surface that preceded deposition as a result of thermal aging. These deposits are typically porous and diminish heat transfer efficiency. The scale layer establishes a diffusion barrier, which can cause a corrosive concentrating mechanism to occur in systems without pH control as in caustic attack.²¹ As a result externally generated iron oxides can promote the internal generation of scale through a waterside corrosion mechanism.

The major source of iron oxides returned to the boiler is the steam/condensate system. In most cases much of the corrosion product is in particulate form and the concentration in the returning condensate can be quite variable. In many combined cycle cogeneration facilities steam is utilized in plant processes and the condensate is returned to the Heat Recovery Steam Generator. At times this condensate can contain high levels of metal oxides, especially when changes occur in the system such as when a process is returned to service after shutdown. As in the case of most contaminants, minimizing the amount of iron oxide entering the boiler is the most important step in controlling its deposition within the boiler.

Some Modes of Failure in HRSGs

A number of failures have been identified in economizers and in the low pressure generating sections of HRSG's following a flow accelerated corrosion mechanism.

Failures have also been observed in intermediate and high pressure sections of some HRSG's following under deposit corrosion mechanisms.

In a number of cases both issues have been identified in the same unit. In these cases it is likely that the flow accelerated corrosion leading to metal loss in the low pressure section and /or the economizer section contributed to the accumulation of iron oxide based deposits in the intermediate and high pressure generating sections of the unit. The remainder of the iron oxide based contamination results from corrosion in the condensate system and from oxygen corrosion in the boiler feedwater system.

Performing routine testing for dissolved and suspended iron in the high pressure boiler water and the boiler feedwater is recommended to provide an indication of the extent of contamination in the boiler feedwater and also the rate of the metal loss in the economizer. These measurements can be used to provide an estimate of the impact of changes made to ameliorate the problem of metal loss in the economizer.

In cases where a failure has occurred a failure analysis investigation is initiated to determine the root cause.

Investigation of Tube Failures

The failure analysis of a boiler tube is quite often a complicated exercise involving the evaluation of many different factors. For example, the types of HRSG tube failures under review can result from thermal effects, such as rapid overheating, long term overheating, thermal stress, waterside chemical effects, such as stress corrosion cracking, caustic attack, hydrogen embrittlement, oxygen corrosion, or under deposit corrosion mechanisms.

The identification of the cause of the failure generally requires more than a simple examination of the failed metal specimen, although such examination is an important component of the identification of the mechanism. In practice, three areas should be investigated in detail to obtain a successful conclusion.

1. A thorough examination of the design of the piece of equipment in question.
2. A thorough examination of the surface of the failed component with complete analysis of any surface deposits observed and a thorough metallographic analysis of both the area of failure and a section of material well removed from the area of failure, showing no signs damage or stress.
3. A thorough examination of the operation of the piece of equipment, including such physical parameters as temperature, pressure firing rate, load changes, or process changes, along with a detailed evaluation of waterside and process side chemistry.

These principles form the basis for a failure analysis investigation.

Laboratory Evaluation of a Failed Boiler Tube Specimen

The tube samples received in the laboratory for failure analysis are first examined visually, both externally and internally, with the aid of a low power stereomicroscope, and photographed. The sample is then sectioned longitudinally to permit close examination of the internal surfaces. A generating tube from a HRSG often has deposition. A longitudinal cut is generally made to section the tube into two halves. Separate areas are then cleaned from surfaces on both sides to permit the calculation of deposit weight density from each. The two deposit samples thus obtained are subjected to full chemical analysis.

The x-ray fluorescence technique is used to determine quantitatively the overall composition of elemental species within the deposit, and x-ray diffraction is used to identify the crystalline species present.

After the deposit weight determination, the two samples are again visually examined utilizing the low power microscope to see if any evidence of underdeposit corrosion can be observed.

Segments are removed from around damaged areas of the tube wall and from an unaffected area removed from the area of failure. These sections are mounted in Bakelite molds and ground and polished in accordance with standard metallographic procedures per ASTM E32-95. The resulting samples are examined with a metallurgical microscope to evaluate the microstructure at the site of concern and compare the condition with the undamaged specimen from the remote location.

In addition sections from the tube wall are examined utilizing a scanning electron microscope equipped with an energy dispersive x-ray analysis system (EDAX). This permits a much more detailed examination of the tube surface under the deposit together with the identification of elemental species at specific locations within the deposit. This analysis can often provide additional clues as to the failure mechanism. For example, the finding of sodium salts in the deposit provides a clue that boiler water was concentrating to high solids values in those areas, indicating the potential for caustic corrosion at the surface.

Scanning Electron Microscope

A Scanning electron Microscope (SEM) equipped with x-ray microanalysis using Energy Dispersive Spectroscopy (EDAX) offers an ideal surface analysis tool that is capable of performing both physical (surface morphology) and chemical (elemental distribution) analysis. As a consequence, the SEM/EDAX x-ray system meets the requirements for surface analysis of boiler tube failures.

Unlike optical microscopy, SEM employs an electron beam instead of a light beam to observe the sample. Since the electron beam has a very small wavelength ($0.1 \sim 0.2 \text{ nm}$), typical resolution of $3.5 \sim 5 \text{ nm}$ can be easily achieved. This fine resolution allows a high magnification up to 100,000X. Furthermore, the combination of the small aperture and the short wavelength of the electron beam results in tremendous depth of field, which allows a large surface to be observed. The interaction of the electron beam with the sample under observation causes characteristic x-rays to be generated from the

region of interest. With an x-ray analyzer, one can determine the elemental makeup of the surface under investigation.

In the SEM units utilized the electron beam is generated from a tungsten filament. The as-received steel tube samples are mechanically cross-sectioned and air cleaned. Cross sections can be either embedded in epoxy resin, polished to 600 grit surface finish, and sputter coated with a layer of gold/palladium to minimize charging, or used as cut.

The secondary electron (SE) images and the backscattered electron (BSE) images of the surface area under study are micrographed. Secondary electrons are generated near the surface and generate topographical details. Backscattered electrons are generated deeper under the surface and yield reliable chemical information. BSE generation depends on the atomic number; the higher the atomic number, the more BSE to analyze. Consequently, elements with higher atomic numbers result in a brighter image. Upon the registration of the image, digital x-ray mapping is activated to identify the distribution of elements. In performing digital x-ray mapping, the spots are illuminated sequentially with the selected energy (normally 20 kV), and the counts of each of the energy bands corresponding to the interested elements are accumulated and registered. The intensity of signals (each element is assigned with a color) corresponds to the concentration of the elements.

Failure Analysis Summary

The investigation of the boiler tube failure follows a series of steps each designed to answer specific questions.

1. Physical evaluation of the sample, such as the condition of the internal and external surfaces, the presence or absence of deposits, and the evidence of corrosion or erosion mechanisms reducing the tube wall thickness are determined.
2. The deposit weight determination quantifies the extent of the deposition present on the waterside surfaces.
3. The deposit analysis provides specific information on the composition of the deposit, which can be correlated with data on boiler feedwater contamination, the water treatment program chemistry, and the composition of the tube steel.
4. The metallographic examination of the tube sample provides information on the composition of the tube steel, the temperature to which the tube wall has been exposed, the morphology of the tube metal in the failure area, and the mechanism of failure.
5. The examination utilizing the scanning electron microscope provides detailed information on the surface conditions in the area of failure and on the spatial location of components of the deposit.
6. The review of the boiler test logs from the plant provides information on fluctuations in boiler feedwater, boiler water, and condensate chemistry.

7. The review of the previous year of boiler operation provides information on boiler load, load swings, shutdown periods, and mechanical maintenance issues.

From a detailed review of all of this information, the mode or mechanisms of failure generally can be established and a reasonable explanation of the events leading to the failure can be developed. Steps can then be taken to ensure that the failure does not recur.

Three cases are discussed to illustrate failures observed in three different systems.

Case Study 1

A Heat Recovery Steam Generator (HRSG) was utilized to provide power generation and process steam in a manufacturing facility. In this unit steam was generated at 950 psig (6.55 Mpa), 450 psig (3.103 Mpa) and 50 psig (0.345 Mpa) in three separate generating sections.

A failure was experienced in one of the generating tubes at the front of the high pressure section. A sample of the tube from the area of failure was provided and a failure analysis was requested. A description of the system is provided in **Table 3**.

Boiler Water Treatment Chemistry

The boiler water treatment program in use in the HRSG was a coordinated phosphate pH control program with a dispersant added to maintain clean waterside conditions and provide transport for feedwater iron contamination through the unit. The products in use are listed in **Table 4**.

The treatment approach was selected to buffer the pH in the boiler water and to provide some ability to accept minor upsets in boiler feedwater quality in terms of hardness, silica, or iron contamination while maintaining clean heat transfer surfaces in the three generating sections in the HRSG.

Examination of the Tube Sample

The tube sample was first examined externally and then sectioned into halves. On the external surface a small hole about 5 mm (0.15 in) in diameter was noted at the area of failure. The hole was located in the upper half of the tube sample. The internal surfaces were examined in detail with the aid of a low power stereo zoom optical microscope and photographed.

A significant amount of deposit was noted on the internal surfaces. The quantity of deposition was significant. The scale thickness was over 4 mm (0.13 in), though a full metallographic examination later showed that this deposit did not contribute to overheating of the tube surface. The inside diameter scale layer in the different regions on the interior of the tube was analyzed utilizing a scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrographic analysis system (EDAX).

The internal surface was cleaned using the bead blast method (per NACE Standard TM0199-99). The deposit weight density measurement obtained was 638 g/ft² on one side of the tube and 743 g/ft² on the side where the hole was observed.

The deposit samples were found to consist primarily of iron oxide as magnetite and hematite together with some phosphate and metallic copper (**Tables 5 and 6**).

Examination of the internal tube surface after cleaning revealed the presence of a series of depressions underneath the deposit slightly off center in the upper portion of the tube sample. The contours of the depressions were relatively smooth showing uneven metal loss with rolling contoured edges.

The samples were examined visually and at magnifications up to 40x with the aid of a stereoscopic microscope. A section was cut from the upper half tube sample to represent the area of failure and approximately 180° of the tube wall.

Additional transverse sections were cut to represent a 180° profile of the tube and the gouged area. The specimens were mounted in epoxy molds and were prepared in accordance with standard metallographic procedures. Each sample was examined in both unetched and etched conditions at magnifications up to 1000x.

Mechanism of Failure

The metallographic analysis found that the cause of the metal loss and eventual failure was caustic corrosion or caustic gouging. This resulted in the direct removal of iron from the surface of the tube in an area where steam bubbles were not being effectively removed from the surface due to the presence of the deposit. In the presence of the deposit water permeates to the surface by capillary action where it is evaporated with the steam being released through the deposit. This allows for the accumulation of boiler water solids at the tube surface in highly concentrated form.

Boiler water concentrated at the tube surface under the deposit leads to very high local concentrations of sodium hydroxide. In this case this resulted in the direct dissolution of iron as ferrate salts from the tube surface leading to the depressions observed. Eventually the tube metal thins to the point where it can no longer withstand boiler pressure and a small disc of metal blows out from the wall of the tube producing the irregular hole observed at the point of failure.

Conclusions

1. Significant metal loss had occurred under the deposit in the upper area of the tube sample.
2. The condition of the tube strongly suggested that metal loss was due to caustic gouging following the concentration of boiler solids at the tube surface due to a concentration boiling mechanism under the deposit.
3. The condition was aggravated due to the heavy deposition on the internal surface of the tube. Significant metal loss has been noted in the economizer in this unit due to a flow accelerated corrosion mechanism. The iron removed from the economizer would be transported directly into the high pressure generating section of the unit contributing to deposit accumulation in this area.

4. The concentration could not have occurred simply due to excessive heating of the tube surface because the external surface of the tube showed no physical indication of an overheating mechanism. Therefore, inadequate washing of the tube surface due to the presence of the deposit is suggested as the major cause of the concentration boiling.
5. The observation of sodium, potassium, and phosphorus in the deposit from the gouged area along with iron and copper provides additional evidence supporting the conclusion that caustic corrosion following the concentration of boiler solids at the tube surface was the primary cause of metal loss in this case.

Recommendations

1. The failed generating tube in the front section of the high pressure generating bank had been replaced.
2. A detailed examination of the high pressure generating bank utilizing the videoprobe was recommended to identify areas of deposition.
3. Plant personnel opted for replacement of the tubes in dirty areas of the high pressure generating bank to eliminate the potential for further failures.
4. The elimination of deposits at the surface of the generating tubes was essential to eliminate metal wastage.
5. Some adjustments to boiler water chemistry were made to maintain strict congruent phosphate pH control with hydroxide or hydrate alkalinity maintained at 0 to (-5.0) mg/L (ppm). This involved changing the coordinated phosphate control regimen to utilize a congruent phosphate pH control approach.

Case Study 2

A Heat Recovery Steam Generator (HRSG) was utilized to provide power generation and process steam in a manufacturing facility. In this unit steam was generated at 1500 psig (10.343 MPa), 250 psig (1.724 MPa) and 35 psig (0.241 MPa) in three separate generating sections.

A failure was experienced in a tube at the front of the low pressure generating section. A section of the tube from the area of failure was provided and a failure analysis was requested. A description of the system is provided in **Table 7**.

Boiler Water Treatment Chemistry

The boiler water treatment program in use in the HRSG was congruent phosphate pH control. Carbohydrazide is added to minimize oxygen contamination in the boiler feedwater and neutralizing amines are utilized to elevate the pH of the boiler feedwater and steam condensate. The products in use are listed in **Table 8**.

The treatment approach was selected to buffer the pH in the boiler water. Careful control of boiler feedwater quality in terms of hardness, silica, or iron contamination was utilized to maintain clean heat transfer surfaces in the three generating sections in the HRSG.

Examination of the Tube Sample

The tube sample was first examined externally and then sectioned into halves. On the external surface a small hole about 8 mm (0.24 in) in diameter was noted at the area of failure. The hole was located in the center of the tube sample. The internal surfaces were examined in detail with the aid of a low power stereo zoom optical microscope and photographed.

No deposit was noted on the internal surfaces. The internal surface was smooth and shiny with no observable magnetite film. A full metallographic examination later showed an absence of oxide deposit on the internal tube surface

The internal tube surface was uniformly thinned to less than 1 mm (0.03 in) in the area of failure. The internal surface was smooth showing a very even pattern of metal loss.

The samples were examined visually and at magnifications up to 40x with the aid of a stereoscopic microscope. A section was cut from the upper half tube sample to represent the area of failure and approximately 180° of the tube wall.

Additional transverse sections were cut to represent a 180° profile of the tube and the gouged area. The specimens were mounted in epoxy molds and were prepared in accordance with standard metallographic procedures. Each sample was examined in both unetched and etched conditions at magnifications up to 1000x.

Mechanism of Failure

The metallographic analysis found that the cause of the metal loss and eventual failure was erosion corrosion coupled with flow accelerated corrosion. This resulted in the direct removal of iron from the internal surface of the tube.

Similar conditions were observed on the internal surfaces of other tube sections removed from the front of the low pressure generating bank. A fine dense black magnetite film was observed the lower area of each tube. The film thinned and finally disappeared about 15 feet from the top where the tube penetrated the upper header. Tube wall thickness measurements performed on tubes further back in the generating bank showed minimal metal loss.

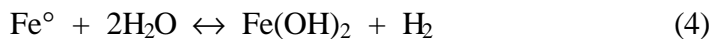
Additional ultrasonic thickness tests revealed areas of metal loss on the top of the first two upper headers in the low pressure generating bank. The header wall thickness was reduced by as much as 30% in some areas.

Millipore filter tests over the previous year showed high concentrations of magnetite in particulate form in the recirculating boiler water in the low pressure section of the unit. Total iron residuals in the boiler feedwater varied between 0.01 mg/L and 0.024 mg/L over the previous year. The

suspended iron residuals in the boiler water varied between 3.7 mg/L and 14.2 mg/L over the same time period. The system operated at between 35 and 55 cycles of concentration so the contribution of feedwater iron to the iron residual observed in the boiler water was between 0.5 and 2.5 mg/L. This indicates that a significant proportion of the particulate iron observed in the low pressure boiler water resulted from corrosion in the low pressure system.

It appears likely in this case that flow accelerated corrosion resulted in the direct removal of iron from the tube surface. This probably results from the rate of steam generation in the first few rows of tubes in the low pressure generating section. The velocity increases rapidly as the fluid (steam/water mixture) rises up the tube, due to the volume occupied by the steam at low pressure. In this case at 35 psig (0.241 MPa) one pound of steam occupies 8.51 cubic feet (0.241m³) while one pound of water occupies 0.016 cubic feet (0.000453 m³). If 10 % of the water passing through the tubes in this 35 psig (0.241 Mpa) circuit is converted to steam the volume of 100 pounds (45.36 kg) of the fluid will increase from 1.67 cubic feet (0.0473 m³) to 86.6 cubic feet (2.453 m³) an increase of almost 5185%. So the steam generated in the tube produces a large increase in fluid volume and hence fluid velocity as the fluid rises up the tube.

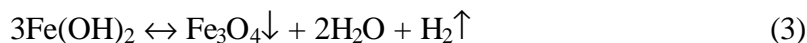
The basic reaction of iron and water under alkaline conditions produces iron hydroxide was shown in equation (4):



The Schikorr mechanism for the formation of magnetite was reviewed earlier in this discussion. This mechanism illustrates that the formation of magnetite at the tube surface occurs in three distinct steps. The second step involves the formation of ferrous hydroxide as shown in equation (2):



In this process, it has been shown that the formation of the ferrous hydroxide (Reaction 2) is the rate determining step. Therefore, the solubility and stability of this reaction product is the key to corrosion protection in the boiler³. The precipitation of ferrous hydroxide at the tube surface is required in step 2 in order to permit the formation of magnetite in the third step.



If the ferrous hydroxide is swept away from the tube surface before precipitation occurs then precipitation and magnetite formation may occur in the bulk solution leading to the dissolution of additional iron from the surface of the tube as portrayed in reaction (1):



This process would explain the relatively high concentrations of magnetite found in the recirculating boiler water.

The particulate magnetite in the boiler water will be abrasive to internal metal surfaces and would potentially accelerate the rate of metal loss from the tube surface by erosion. In addition the particulate magnetite impinging on the upper surface of the header will lead to an erosion corrosion

effect in that area. That would provide an explanation for the metal loss from the upper surface of the headers.

Conclusions

1. Flow accelerated corrosion probably contributed to the metal loss from the upper area of the tubes in the front of the low pressure generating bank.
2. The presence of high concentrations of magnetite in the boiler water in the low pressure system at least partly resulted from the flow accelerated corrosion mechanism.
3. The particulate iron in the low pressure boiler water contributed to the erosion corrosion mechanism, which resulted in the tube failure observed.

Case Study 3

At a Midwestern chemical plant steam was generated at 600 psig (4.482 Mpa) and 399 °C (750 °F) for power generation and process use.

Steam line cracking was observed after about four years of service in a steam turbine exhaust line located downstream of a desuperheating inlet. Steam is supplied at 600 psig (4.482 MPa) and 399 °C to the turbine. The steam pressure is reduced to 150 psig (1.034 Mpa) at the exhaust point. Boiler feedwater is used for desuperheating the exhaust steam.

Examination Procedure:

Sections from the steam line were submitted for failure analysis in an effort to help identify the cause of cracking. The material of construction was reported to be SA 516 grade 70 carbon steel and this was confirmed by analysis.

Multiple cracks oriented both parallel and transverse to circumferential welds were observed. Field weld repairs had been made but were not completely successful. The piping sections were wire brushed and examined using dry magnetic particle inspection techniques and photographed. Samples containing cracks were dry cut and prepared for metallographic examination by mounting, grinding, polishing and etching in accordance with standard metallographic procedures per ASTM E3-95.

Several crack-containing samples were fractured open and examined using a scanning electron microscope (SEM). Fracture surface deposits near crack termination points were analyzed using energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS) to determine elemental composition. Bulk I.D. deposit samples were also analyzed by powder X-ray diffraction (XRD) to determine crystalline compound constituents.

Examination Results:

The photomicrographs showed a close up view of numerous cracks that were transverse to the circumferential welds. The cracks were found in many locations. Many of the indications were through-

wall. The cracks were deposit filled and primarily transgranular. The cracks showed some branching, and there were occasional corrosion projections off the primary crack paths.

Analyses of the bulk I.D. deposits showed primarily magnesium silicate hydrate/serpentine and iron oxide/magnetite, calcium carbonate/calcite, and magnesium hydroxide/brucite.

The deposits within the cracks contained primarily sodium, chlorine, and sulfur even though these elements were only found in trace or non-detectable amounts in the bulk deposits.

Conclusions from the Analytical Data:

1. The cracking observed in the piping sections was indicative of caustic-induced stress corrosion cracking (SCC) ²².
2. The stress corrosion cracking was identified by the cracking morphology, (deposit-filled and primarily transgranular), plus the presence of major amounts of sodium at the crack terminus areas.
3. Caustic entering the piping and concentrating into crevices and cracks through evaporation or wet/dry episodes had apparently occurred.

Investigation:

Even though the initial failure did not occur until after four years of operation, additional failures began occurring on a frequent basis and as quickly as within six days after new piping replacement.

Stress corrosion cracking is insidious since it is often unpredictable in nature and a metal can suddenly crack without any previous warning. SCC is a progressive fracture mechanism in metals that is caused by the simultaneous interaction of corrodent and a sustained tensile stress. The stress may result from applied external load or it may be residual due to the pipe manufacturing process, heat treatment, welding, grinding, or assembly.

In this case, the primary corrodent was identified as sodium hydroxide. Efforts were directed at reducing the caustic content of the steam and static stress on the piping.

Since the initial cracking took four years to occur, then subsequent failures occurred in only days, there was some suspicion that higher external stress levels were being placed on the replacement pipe. Care was taken to make sure that pipe sections and installation did not add undue external stress. To minimize stress, shot peening was performed on replacement piping, but this did not eliminate cracking. In efforts to determine stress in the piping, measurements were made at the failure analysis laboratory using a computer modeling technique. The piping stress analysis indicated that the stresses were relatively low. The final piping section that was installed was measured very precisely to avoid any external applied stress.

Sources of Sodium:

The makeup water to the boiler is provided from separate counter-current packed bed demineralizer units. The system includes a vacuum degasification stage prior to entering the

demineralizer storage tank. Neutralizing amine is added to raise the pH before the water is preheated and enters the deaerator. Sodium sulfite was applied at the storage section of the deaerator. This was a factor contributing sodium to the steam, since boiler feedwater is used for desuperheating. The calculated contribution of the sulfite to sodium in the feedwater was found to be small, however, the application point for the sulfite was changed to the feedwater line downstream of the desuperheater supply.

The demineralizers were regenerated based upon conductivity, and silica analyses were performed manually. No continuous steam analyzers were in place. A regimen of sodium testing on the demineralizers, feedwater, and steam was initiated and results showed high sodium levels out of the cation unit and anion unit from one of the trains. During the service cycles the sodium was found to be in the 1 – 4 mg/L range and as high as 63 mg/L immediately after regenerations.

Continuous conductivity analyzers with graphing capability were installed on each demineralizer train and the boiler feedwater to quantify the size and duration of upset conditions. The monitoring has also allowed plant personnel to react more quickly to upset conditions.

Feedwater sodium residuals were found to be typically in the 0.3 – 2.0 mg/L range. Sodium residuals in the steam after desuperheating were 0.1 – 0.9 mg/L.

To reduce sodium from the demineralizers the cation resin was replaced which lowered sodium levels out of the cation units to <0.1 mg/L. Also to improve regeneration efficiency and to reduce sodium leakage, the two-step sulfuric acid feed was changed from 1% / 3% to 1% / 4%. In addition a longer pre-rinse time was initiated for the cation units.

Inspection of steam separation equipment showed some damage, so repairs were made to minimize boiler water carryover.

Another suspected area of caustic contamination was from the CIP (Clean-In-Place) system. Steam line supply check valves were replaced due to the potential for them to allow caustic to enter the steam piping under some conditions.

Many of the changes were made as soon as they could be implemented, so a cause and effect solution was difficult to determine. The main objective was to eliminate or at least reduce the frequency of failure as quickly as possible. However there were some quantifiable changes:

1. Replacing the cation resin, changing the sulfuric acid strength, and increasing pre-rinse time reduced the sodium concentration out of the cation units to typically <0.05mg/L and minimized high level spikes.
2. Sodium in the steam was reduced from 0.9 mg/L to <0.1 mg/L by making repairs to the steam separation equipment.
3. Sodium contribution in the feedwater was reduced to <0.1 mg/L by changes made to the demineralizer, changing the sodium sulfite feed point, and repairing the steam separation equipment.

Conclusions:

1. Caustic-induced stress corrosion cracking can occur suddenly to steam line piping if the conditions for stress and caustic concentration mechanisms are in place.
2. Sodium levels should be closely monitored and held to minimal levels to reduce the risk.
3. Care should be taken to minimize stress to the material; and wet/dry conditions should be avoided.
4. Cracking was curtailed after stress and caustic levels were lowered to below the apparent critical point.

SUMMARY

Three different types of failure mechanisms in steam generating equipment have been discussed. Cases of flow accelerated corrosion related failures and failures resulting from deposit accumulation have been noted with increasing frequency in HRSG units.

1. A number of failures have been identified in economizers and in the low pressure generating sections of HRSG's following a flow accelerated corrosion mechanism.
2. Failures have also been observed in intermediate and high pressure sections of some HRSGs following under deposit corrosion mechanisms.
3. In a number of cases both issues have been identified in the same unit. In these cases it is likely that the flow accelerated corrosion leading to metal loss in the low pressure section and /or the economizer section contributed to the accumulation of iron oxide based deposits in the intermediate and high pressure generating sections of the unit. The remainder of the iron oxide based contamination results from corrosion in the condensate system and from oxygen corrosion in the boiler feedwater system.
4. On occasion failures are identified in steam transmission lines following the use of boiler feedwater for attemperation in desuperheating systems. As a general rule only water of high purity should be used for steam attemperation. In particular the use of feedwater for attemperation should be avoided if it is contaminated with sodium based boiler water treatment compounds
5. The cases illustrate the necessity to closely monitor and regulate the sodium content of boiler feedwater supplied to Heat Recovery Steam Generators.

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Table 1.
Iron Corrosion Reactions

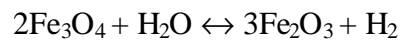
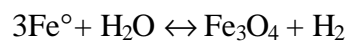
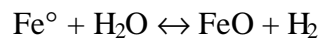
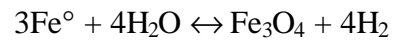
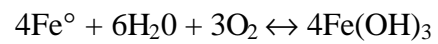
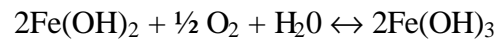
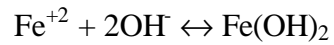
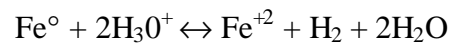
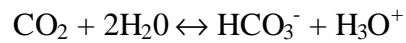
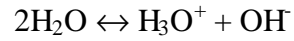


Table 2.**Solubility Product Constants and Additional Information for Iron Containing Species^{12,13,14,15,16}**

| Compound | LOG K _{sp} (25C) | Color | Crystallographic System | Comments |
|---|------------------------------|-----------------|-----------------------------------|---|
| Fe(OH) ₂ | -14 -15.1 | White | ----- (Brucite) | 1) Decomposes @ 100C to Fe ₃ O ₄ + H ₂ 2) Dehydrates to FeO 3) At room temperature + O ₂ can form goethite lepidocrocite and magnetite. |
| Fe(OH) ₃ | -38.7 | ----- | ----- | Unstable iron form rapidly dehydrates to oxide form. |
| FeO (Wustite) | | Black | Cubic (NaCl) | Decomposes to Fe and Fe ₃ O ₄ |
| Fe ₃ O ₄ (Magnetite) | -14 -18 | Black | Cubic (Inverse Spinel) | Oxide typical of "O" oxygen systems. Found in utility condensate systems using hydrazine. |
| Alpha FeO(OH) (Goethite) | -39.1 | Yellow | Orthorhombic | Dehydrates to hematite at 200C. Forms hematite at lower temperatures in presence of H ₂ O. This form is favored at high pH and has been identified by color in condensate systems. |
| Gamma FeO(OH) (Lepidocrocite) | -39.1 | Orange | Orthorhombic | Dehydrates to hematite at 200C. In the presence of H ₂ O converts to hematite at lower temperatures. Has been identified based on color in systems where iron slugging is a problem. Has been mistaken for copper contamination. |
| Alpha Fe ₂ O ₃ (Hematite) | -42.7 | Red to Black | Trigonal (Hexagonal unit cell) | Decomposes to magnetite at 1457C. Most common iron form in Industrial System. Hematite formation favored by low pH and increasing temperatures. |
| OTHER POSSIBLE IRON FORMS | | | | |
| Beta FeO(OH) | | Light Brown | ----- | Dehydrates to hematite at 230C. Presence of water enhances dehydration. |
| Gamma Fe ₂ O ₃ (Maghemite) | | Brown | Cubic (Spinel) | Transforms to hematite above 250C. Presence of H ₂ O enhances transformation. |

Table 3.

Case 1: System Description

Equipment Description

| | |
|-----------------------|---|
| Boiler type | Heat Recovery Steam Generator with 3 Generating Sections. |
| Rated capacity | 52 Kg/s (415,000 lb./hr.) |
| Operating pressure | HP 6.6 Mpa (950 psig); IP 3.1 Mpa (450 psig); LP 0.35 Mpa (50 psig) |
| Superheat | Single stage controlled, 440°C (825°F) |
| Fuel | Natural gas |
| Method of firing | Gas Turbine Exhaust with Duct Burners |
| Gas Turbine | General Electric |
| Deaerator | Spray/Tray type |
| Operating temperature | 120°C (249°F) |
| Operating pressure | 100 Kpa (15 psig) |
| Makeup water | Demineralized |
| Condensate return | 90% |
| Steam use | Turbine generator, absorption refrigeration equipment, process heating, etc. |

Table 4.

Case 1: Boiler Water Treatment Products Utilized

| <u>Product</u> | <u>Use</u> | <u>Concentration Range In Boiler mg/L (ppm)</u> |
|-----------------------------|-------------------------|---|
| Sodium hexametaphosphate | Boiler Water pH control | 10-15 |
| Sodium hydroxide | | 0-5 |
| Diethylhydroxylamine | Oxygen removal | 0.1-0.2 |
| Blended copolymer | Boiler dispersant | 10 30 |
| Neutralizing Amine | Condensate pH elevation | - |

Table 5**Case 1: Report of Deposit Analysis**

| | PERCENT |
|---|---------|
| ZINC as ZnO | NONE |
| COPPER as CuO | 9.8 |
| NICKEL as NIO | 0.5 |
| IRON as Fe ₃ O ₄ | 72.9 |
| MANGANESE AS MnO ₂ | 1.0 |
| CHROMIUM as Cr ₂ O ₃ | NONE |
| TIN as SnO ₂ | NONE |
| TITANIUM as TiO ₂ | NONE |
| ALUMINUM as Al ₂ O ₃ | 0.3 |
| CALCIUM as CaO | 0.2 |
| MAGNESIUM as MgO | 0.1 |
| STRONTIUM as SrO | NONE |
| BARIUM as BaO | NONE |
| SODIUM as Na ₂ O | 1.9 |
| POTASSIUM as K ₂ O | 0.6 |
| COBALT as CoO | NONE |
| CHLORIDE as NaCl | NONE |
| SULFATE as SO ₃ | NONE |
| TOTAL PHOSPHORUS as P ₂ O ₅ (3) | 5.8 |
| SILICA as SiO ₂ | 1.9 |
| CARBONATE as CO ₂ | NONE |
| VANADIUM as V ₂ O ₅ | NONE |
| LEAD as PbO | NONE |
| ARSENIC as As ₂ O ₃ | NONE |
| CORRECTED IGNITION LOSS | 3.8 |
| UNDERTERMINED | 1.2 |
| TOTAL | 100 |

TABLE 6**Case 1: Report of Deposit Analysis**

| | PERCENT |
|---|---------|
| ZINC as ZnO | NONE |
| COPPER as CuO | 7.4 |
| NICKEL as NIO | 0.9 |
| IRON as Fe ₃ O ₄ | 69.1 |
| MAGANESE AS MnO ₂ | 0.3 |
| CHROMIUM as Cr ₂ O ₃ | NONE |
| TIN as SnO ₂ | NONE |
| TITANIUM as TiO ₂ | NONE |
| ALUMINUM as Al ₂ O ₃ | 0.1 |
| CALCIUM as CaO | 1.3 |
| MAGNESIUM as MgO | 0.3 |
| STRONTIUM as SrO | NONE |
| BARIUM as BaO | NONE |
| SODIUM as Na ₂ O | 4.6 |
| POTASSIUM as K ₂ O | 1.7 |
| COBALT as CoO | NONE |
| CHLORIDE as NaCl | NONE |
| SULFATE as SO ₃ | 0.2 |
| TOTAL PHOSPHORUS as P ₂ O ₅ (3) | 10.1 |
| SILICA as SiO ₂ | 0.1 |
| CARBONATE as CO ₂ | NONE |
| VANADIUM as V ₂ O ₅ | NONE |
| LEAD as PbO | NONE |
| ARSENIC as As ₂ O ₃ | NONE |
| CORRECTED IGNITION LOSS | 2.7 |
| UNDERTERMINED | 1.2 |
| TOTAL | 100 |

Table 7

Case 2: System Description

Equipment Description

| | |
|-----------------------|--|
| Boiler type | Heat Recovery Steam Generator with 3 Generating Sections. |
| Rated capacity | 115.6 Kg/s (923,000 lb./hr.) |
| Operating pressure | HP 10.4 Mpa (1500 psig); IP 1.7 Mpa (250 psig); LP 0.25 Mpa (35 psig) |
| Superheat | Single stage controlled, 540°C (1004°F) |
| Fuel | Natural gas |
| Method of firing | Gas Turbine Exhaust with Duct Burners |
| Gas Turbine | General Electric |
| Deaerator | Spray/Tray type |
| Operating temperature | 123°C (255°F) |
| Operating pressure | 113 Kpa (17 psig) |
| Makeup water | Demineralized |
| Condensate return | 85% |
| Steam use | Turbine generator, absorption refrigeration equipment, process heating, etc. |

Table 8.

Case 2: Boiler Water Treatment Products Utilized

| <u>Product</u> | <u>Use</u> | <u>Concentration Range In Boiler mg/L (ppm)</u> |
|----------------------|-------------------------|---|
| Disodium phosphate | Boiler water pH control | 8-12 |
| Monosodium phosphate | Boiler water pH control | 8-12 |
| Carbohydrazide | Oxygen removal | 0.1-0.2 |
| Neutralizing Amine | Condensate pH elevation | - |