RECOVERY BOILER WATER TREATMENT

Robert D. Bartholomew, P.E.

Associate

Sheppard T. Powell Associates, LLC

1915 Aliceanna Street

Baltimore, Maryland USA 21231

ABSTRACT

Failures of tubes in the lower furnace of recovery boilers can lead to smelt/water explosions. Waterside deposits in boiler tubes raise tube metal temperatures and can lead to damage or tube failures from overheating and both waterside and fireside corrosion. Waterside corrosion and tube failures can result from low or high pH values in the boiler water. Recovery boiler operators need to monitor and control steam/water cycle chemistry to protect recovery boilers and turbines. These and other aspects of a comprehensive steam/water cycle chemistry program are presented and explained.

PRESENTATION OVERVIEW

Figure 1 presents an overview of the recovery boiler water treatment program. In order to prevent recovery boiler tube failures, turbine deposits and corrosion of other steam/water cycle components, one should understand the steam water cycle design and significance of common types of chemistry monitoring. A critical failure is one that is likely to cause a smelt water explosion and a noncritical failure is one that is not likely to cause an explosion.

Figure 1 - Presentation Format

- Primary Goals for Recovery Boiler
  - Prevent Critical Tube Failures (C.T.F.)
  - Prevent Noncritical Tube Failures (N.C.T.F.)
- Secondary Goals for Rest of Steam/Water Cycle Components
  - Avoid Deposits on Steam Turbine from High Boiler Water Silica or Carryover
  - Control Steel and Copper/Copper Alloy Corrosion of and Corrosion Product Transport from Dryers, Heaters, Condensers, Condensate Lines, etc.,
- Steam/Water Cycle: Basic

- Top Routine Chemistry Parameters
- Summary
- Objectives of the Treatment Program

This conference demonstrates that there are many areas of the Kraft Recovery Boiler cycle that demand your attention. Water treatment is no exception. The primary objectives of the treatment program are listed in Figure 2:

Figure 2 - Objectives of Treatment Program

Component	Deposition	Corrosion
Condensate System	--	Minor
Feedwater System	--	Minor
Economizer Tubes (N·C·T·F·)	Minor	O or Minor
Boiler (C·T·F·)	<20-25 g/ft^2	O or Minor
Superheaters	O	O
Turbines	O	O

The economizer was added as a separate line in 2017 because many of the noncritical tube leaks reported to the Black Liquor Recovery Boiler Advisory Committee BLRBAC continue to be in economizers (typically at welds in the bottom row tubes). Stress assisted corrosion (SAC) and oxygen pitting have been cited as the root causes of the damage. A good recovery boiler water treatment program must control dissolved oxygen in the feedwater at low levels (<10 ppb) to minimize the potential for economizer damage and tube leaks. Figure 3 provides a summary of chemistry related economizer tube failures.

Figure 3 – Chemistry Related Economizer Failures

- Main Failure Mechanisms
  - Stress Assisted Corrosion (SAC)
  - Dissolved Oxygen (DO) Pitting
- Primary Chemistry Factors
  - Dissolved Oxygen (SAC and DO Pitting)
  - Low Feedwater pH (SAC)
  - Dissolved Solids (DO pitting usually only occurs in economizers receiving softened makeup)

Waterside deposits in waterwall tubes raise tube metal temperatures and can lead to tube failures from overheating and waterside and fireside corrosion. This is summarized in Figure 4.

Figure 4 – Common Chemistry Related Waterwall Tube Failures

- Underdeposit Waterside Corrosion
- Overheating Due to Heavy Waterside Deposits
- Fireside Corrosion Due to Heavy Waterside Deposits

Waterside corrosion can result from low or high boiler water pH values and high levels of certain salts. Tube failures in the lower furnace can cause deadly explosions from smelt-water reactions. Figures 5-7 present examples of waterwall tube deposits, overheating, and corrosion in an oil fired boiler, coal fired boiler, and a black liquor recovery boiler, respectively (from three separate mills).

Figure 5 - Boiler Deposit Example



During operation, the tube in Figure 5 was filled with water and heat was passing from the furnace (top of photograph) through the tube wall and deposit layer to the boiler water to generate steam. Since the deposits insulate the tube from the water, the tube wall becomes hotter as deposits accumulate. If the tube gets hot enough, the metal starts to soften and the internal pressure causes the tube to blow up like a balloon (called a blister) and fail.

The particular tube shown in Figure 5 was from a nose tube of a pulp mill power boiler. Nose tubes are sloped tubes in the middle to upper furnace that often accumulate localized deposits. However, the heat flux in this tube in this particular boiler was obviously fairly low because the tube did not overheat and fail. Tubes in other boilers have failed due to short term overheating from a quarter of the deposits shown in Figure 3. Carbon steel tubes with heavy deposits in the lower furnace of black liquor recovery boilers usually will experience severe fireside corrosion and failure well before they will actually experience an overheating failure.

Figure 6 presents an internal view of a coal fired boiler tube that had severe waterside deposits about 1-2 feet over the firing grate, and the tube failed due to short-term overheating (blistering) on the hot side surface. The boiler experienced a rash of failures and had to be chemically cleaned on an expedited schedule. The oval areas with shadows are the locations where the tube had expanded due to the high localized temperatures and internal pressure.

Figure 6 - Boiler Blistering Example

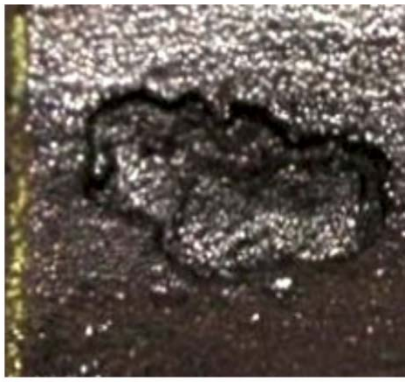


Figure 7 shows a patch of localized deposit on the waterside tube surfaces in a recovery boiler waterwall tube which had significant underdeposit corrosion.

Figure 7 - Boiler Corrosion Example



● Localized patch of waterside deposits after brushing off loose surface deposits.

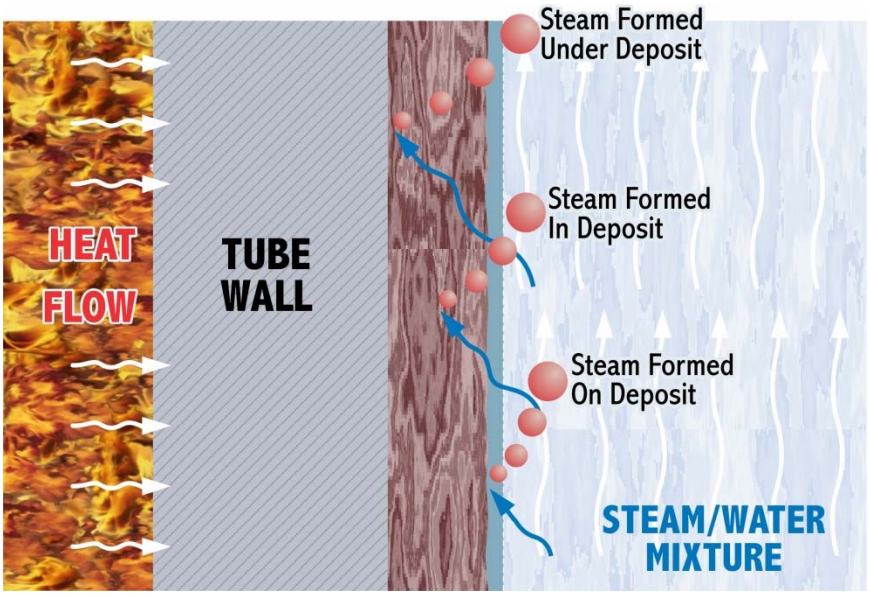


● Underdeposit corrosion revealed after scraping and vibrating off all deposits to base metal.

During operation, the tube metal under the deposits was hot and boiler water that contacted the metal surface boiled. A tube in a boiler behaves just like a frying pan on a stove. If you throw tap water on a hot frying pan, the water boils away and leaves behind a white residue of dried salts. In a boiler, there is a constant flow of water across the tube surface, and the tube surface usually does not completely dry out. However, the boiler water salts do gradually concentrate under deposits to much higher levels than present in the boiler water.

Figure 8 presents a representation of water filtering through deposits and evaporative concentration under deposits. Internal deposits inhibit both the ability of the heat to leave the tube surface and the ability of the water to reach the tube surface to wash away concentrating salts. While the bulk boiler water may be noncorrosive, boiler water can be concentrated to corrosive levels underneath deposits. The extent of concentration depends on the deposit weight, composition and the localized heat flux.

Figure 8 - Evaporative Concentration & Filtering In Deposits



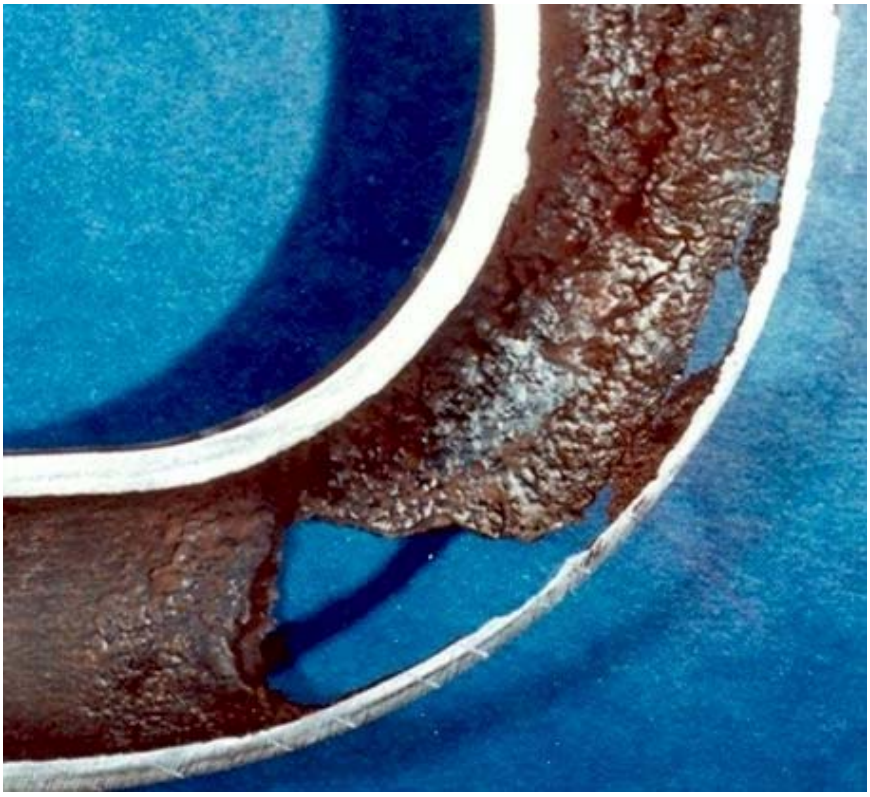
Also, most mills have experienced chemistry upsets. A chemistry upset which may have occurred (or repeatedly occurred) when the boiler was relatively clean may have had little or no effect on the boiler. However, if the boiler now has heavier deposits, the same upset occurring today may cause significant damage and possibly failure of boiler tubes.

While many boilers have operated for a long time without chemical cleaning, most boilers eventually need to be chemically cleaned as a part of routine maintenance to avoid overheating, underdeposit corrosion, or fireside corrosion. Deposits insulate tubes, which raises tube temperatures, and can lead to short-term (blisters) and long-term (creep) overheating, waterside and fireside corrosion.

Corrosion control in the steam, condensate, and feedwater system equipment is a primary water treatment objective both to protect the process equipment itself and to minimize corrosion products transported to the recovery boiler. Some mills have massive surface areas in various process heat exchangers and pipelines (one mill reportedly had 2 miles of copper tubing in their dryers alone). Moderate corrosion in these large surface areas can produce and release large quantities of corrosion products. Also, severe corrosion has caused some of these components to fail prematurely.

The damage in Figure 9 shows a primary superheater which failed after about 6 months of corrosion occurring during operation. This was the first bend in the gas pass in a boiler that was experiencing carryover. This was the second superheater lost on this boiler in 6 months after a boiler water chemistry change from sodium phosphates to potassium phosphates. Plant personnel had not realized the link between the change in treatment and the first superheater failure & replacement - because the original superheater had been in service for a number of years before the chemistry change. After switching back to sodium phosphate treatment, the third superheater lasted at least six years (and probably has lasted longer).

Figure 9 - Superheater Corrosion Example



Deposits on turbines can cause reduced efficiency and reduced capacity. Sometimes salt deposits on turbines, superheaters, and/or steam piping have contributed to corrosion of these components. Susceptible components, such

as stainless steel expansion bellows, can undergo catastrophic failure as a result of deposition from impure steam. Figure 10 presents an example of turbine deposits. The deposits shown in Figure 8 did not actually result in any detectable damage to turbine components. More information on the control of steam purity is available from the ASME (1).

Figure 10 - Turbine Deposits Example



It is hoped that these examples of deposits and corrosion have captured the interest and concern that is necessary to ensure safe and reliable operation of the recovery boiler, power boiler, turbine, and associated components of the steam/water cycle. Maintaining proper conditions and chemistry in steam/water cycle should be a primary responsibility of operations, maintenance and engineering personnel.

INTRODUCTION TO THE STEAM/WATER CYCLE

Figure 11 presents a simplified steam/water cycle diagram. It includes the major components present in most cycles - the treated makeup, makeup storage, a heat-recovery heat exchanger (in this case a blowdown heat exchanger), a deaerator, a feedwater heater (often not present), boiler, condensate collection system, and a condensate filtration and polishing system.

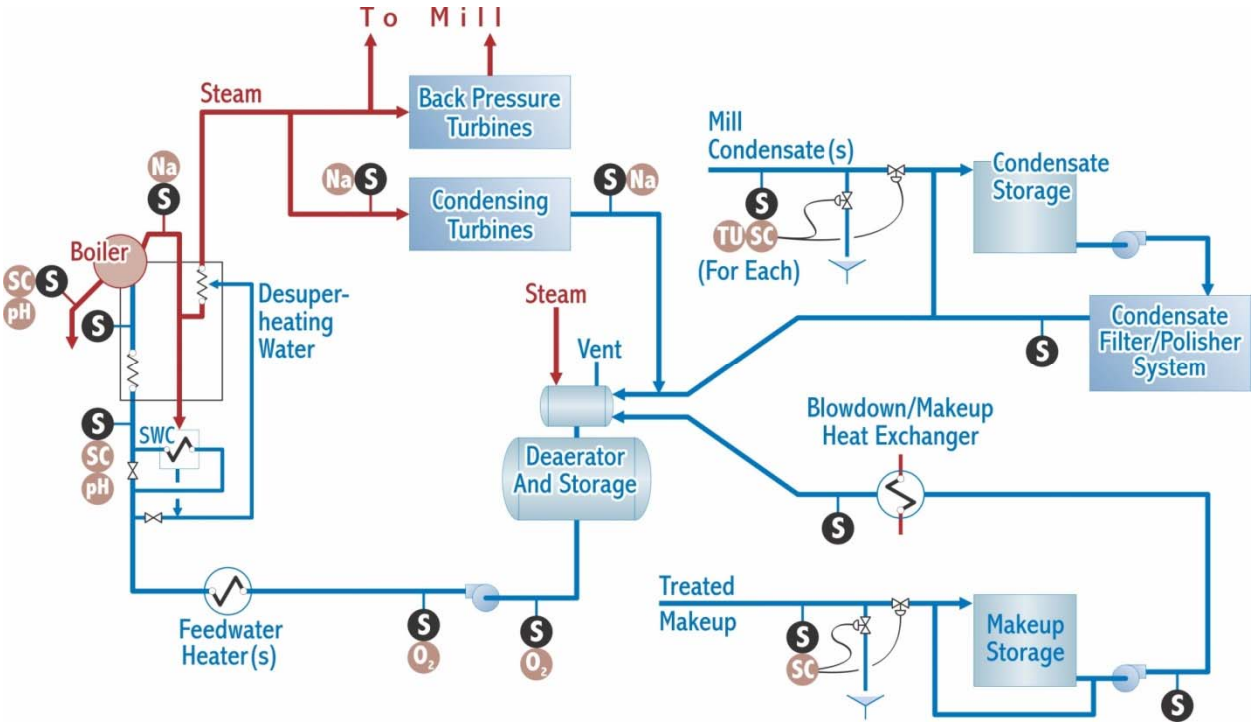
Modern recovery boilers normally are designed for high pressures and have makeup demineralization systems. Demineralization systems remove nonvolatile solids (and carbon dioxide) from makeup water and provide a very low conductivity makeup water supply. Demineralization usually is achieved through ion exchange resins and/or reverse osmosis (RO) membranes. Continuous electrodeionization (CEDI) modules are sometimes used to polish the effluent of RO units.

Makeup softeners use cation resin regenerated with salt to exchange sodium for hardness to produce a low hardness makeup water. Softened makeup generally is used only for older plants with low pressure recovery boilers.

There are several types of condensate polishers. Ion exchange softeners are most common. For condensate applications, these softeners are regenerated with salt (sodium form) or amine solutions (amine form). The amine form is preferred and most common for systems with demineralized makeup. Mixed bed polishers also may be used to demineralize the condensate. This practice typically is limited to facilities with high pressure (>1000 psi) condensing steam turbines.

Several types of condensate filters are in use. The most common are electromagnetic filters and disposable cartridge filters. Precoat filters, backwashable metal mesh filters, and carbon filters also have been used. Use of carbon filters is not advised as the hot condensate has been found to leach significant amounts of materials from the carbon bed. Carbon fines also can leak carbon fines.

Figure 11 – Steam/Water Cycle Diagram



The deaerator removes dissolved oxygen and other noncondensable gases from the condensate and makeup entering the vessel and their design is briefly discussed in a subsequent section.

Blowdown flash tanks and other heat recovery systems should be shown on steam water cycle diagrams as they are potential sources of contamination to the feedwater. Feedwater heaters should be included on cycle drawings because both the tube and shell sides of the heater can introduce corrosion products to the feedwater.

While not shown in our simplified steam/water cycle diagram, it is suggested that the locations and types of process contamination be listed on this or a supplemental condensate collection system drawing to facilitate troubleshooting in an upset. For example, this should include evaporator condensate, glycol heaters, fuel oil heaters, steam surface condensers, etc.

Figure 11 also includes minimum recommended sampling and on-line monitoring. Online monitoring is discussed in the next section.

ONLINE CHEMISTRY MONITORING

In order to understand chemistry in the steam/water cycle, it is useful to define some of the common chemistry readings that may be available to recovery boiler operators from on-line analyzers and grab sample testing. While routine grab sample analyses of select parameters are recommended, they are performed on a limited schedule and should be a supplement, not a substitute, for on-line analyzers in a modern recovery boiler installation. Recommended sample points and online analyzers for the steam/water cycle were listed in Figure 11. The key for this figure is presented below. We have also defined some online analyzers that are commonly used in mills with high pressure turbines.

- **S**: Sample Point Cooled To 25°C (77°F).
- **SC**: Specific Conductivity (often just called conductivity) provides a measure of total conductive dissolved solids (acids, alkalies, and salts). The units of conductivity are reported in microsiemens per centimeter (µS/cm) or micromhos per centimeter (µmhos/cm). These units are identical. When comparing on-line and grab sample readings it is cautioned that modern grab sample instruments often have a feature that automatically switches units from µS/cm to mS/cm, where 1 mS/cm is 1000 µS/cm. Read the fine print on the digital readout - as this can delay proper response during major chemistry upsets. Boiler water can be 20-150 µS/cm, condensate, feedwater and steam can be 2-10 µS/cm, and demineralized makeup can be 0.05 to 5.0 µS/cm, depending on system requirements and capabilities. Plants with softened makeup have much higher values.
- **CC**: Cation Conductivity (also in µS/cm) provides a more sensitive measurement of just the conductive anions present (e.g., carbon dioxide, organic acids, sulfate, and chloride). It consists of a conductivity meter after a cation exchange column that exchanges all cations for hydrogen, which removes residual alkali (e.g., ammonia, amine, sodium) and converts the traces of salts to their acid form. While not shown in Figure 11, it is becoming standard at mills with new high pressure turbines to comply with turbine manufacturer limits. In such facilities, it is typically monitored in steam, feedwater and sometimes condensate streams. Values should be low (e.g., <0.2-0.5 µS/cm) except in upset conditions.
- **pH**: Technically, the pH is -log [hydrogen ion activity]. It is a measure of the relative acidity or alkalinity of a water sample. Values go from the free mineral acid range (e.g., dilute sulfuric acid) with pH values of 0 to 4 up to extremely alkaline pH values of 14 (e.g., caustic soda). A neutral pH is 7, and pH values in the steam/water cycle generally should be in the weak alkali (also called weak base) range (pH 8-10 or pH 8-11).
- **Na**: Sodium (reported as parts per billion or ppb of Na) indicates the amount of caustic soda (NaOH) leaking from the makeup system, or various sodium salts in the feedwater, desuperheating water, and steam.
- **DO**: Dissolved Oxygen (reported as ppb O^2) causes corrosion of copper surfaces in the steam/condensate/feedwater system and can contribute to corrosion of steel surfaces.
- **SiO_2**: Silica (reported as ppb SiO_2 on analyzer). A soluble form of sand that volatilizes from the boiler water and can gradually cause deposits in the tail end of superheat condensing turbines (if above 20 ppb). Excessive levels also can form hard, insulating deposits in boilers. Online silica analyzers are commonly included in makeup demineralization systems using ion exchange to ensure prompt regenerations and minimize the amount of silica entering the cycle. Boiler water silica should be monitored in all mills. Most mills found that grab sample monitoring is sufficient, although online silica monitoring may be used. The primary reason to monitor boiler water silica is to limit silica concentrations in the steam, which results in deposits on the low pressure end of condensing turbines. Also, silicate compounds are sometimes found on waterwall tubes in boilers on softened makeup if silica, hydroxide alkalinity, and other impurities (hardness, aluminum, iron) are not properly controlled.
- **TU**: Turbidity (reported in NTU, nephelometric turbidity unit). An indication of colloidal and suspended matter. It directly measures the light scattered at a 90 degree angle. Turbidimeters calibrated with 100 NTU= 2 mg/L of Formazin were found to be directly proportional to suspended iron oxide (i.e., 100-2000 ppb = 5-100 NTU)(2). This corresponds to 20 ppb of iron oxide per NTU of turbidity - although it may become less linear at lower (<100 ppb) concentrations. Benchtop spectrophotometers cannot actually measure true turbidity, but they often can provide turbidity indications and results are presented in FTU (formazin turbidity unit. Testing by the writer by diluting black liquor from before a concentrator found that 1 FTU corresponded to about 1.5-2.5 ppm of black liquor solids (0.4-0.7 FTU/ppm) whereas the black liquor from the concentrator outlet at another mill resulted in 3-4 FTU/ppm of black liquor solids. At least one mill sewers condensate when the turbidity is over 1 NTU.

- While not shown, plants with persistent problems with hardness in the condensate also may have a total hardness analyzer which measures the calcium and magnesium (usually expressed as ppm as $CaCO_3$). Hardness precipitates in the boiler, forms scales, and can cause low boiler water pH values. Values should normally be less than 0.05 ppm as $CaCO_3$.
- For plants with starch contamination problems, chemical oxygen demand (COD) testing has been found to be useful at detecting contamination. Since it is a nonspecific test, it is suggested to determine baseline readings for the makeup, individual condensate streams, feedwater and boiler water samples during a normal operating period for comparison purposes when chemistry upsets are experienced.

General guidance on sample system design is available in TIP 0416-03 (3). Guidance also is available from ASME (4). For grab or on-line monitoring, a stable sample temperature of 25°C is critical for accurate pH and conductivity measurements and is the basis for limits. Higher temperatures cause low pH readings and higher conductivity readings.

The preceding analyzers have been used for decades, although some were used to a lesser extent in the pulp and paper industry. TIP 0416-03 and its predecessor documents back to 1984 have recommended minimum grab-sample sample frequency of only once per shift, but suggest these on-line analyzers in the footnotes. (3, 5, 6). If a typical grab sample takes one minute to collect, and you have 12-hour shifts, this means that 99.86% of the time you are not monitoring your chemistry. Monitoring once per shift is not adequate without on-line analyzers.

While many mills and power plants have survived in the past for years with little or no on-line monitors and monitoring only once per shift, some have found out the hard way that intermittent grab sampling can be wholly inadequate in upset conditions. Facilities that rely on grab samples may have had old boilers and turbines, in which the designs were very forgiving to chemical contamination. Other facilities have been just plain lucky.

If your plant does not have these sample points, adequate sample conditioning systems, and on-line analyzers, it is suggested that you consider adding them to your short or long-term steam/water cycle improvement plan. Of these, the sample conditioning system must be completed first or the on-line analyzers will provide faulty readings and may be prematurely damaged.

TOP ROUTINE CHEMISTRY TESTS

While improvements in the on-line monitoring program are advised, routine grab sample testing remains a standard practice in the industry. Understanding some of these basic chemistry parameters is necessary to effectively control feedwater and boiler water chemistry. Figure 12 presents just some of the top chemistry tests due to the limited time of this presentation.

Figure 12 - Top Routine Chemistry Tests

- Specific Conductivity
- pH
- Dissolved Oxygen and/or Scavenger
- Hardness
- Phosphate

Online or routine monitoring of color, Turbidity, Silica, Iron/Copper Corrosion Products, Sodium, and Alkalinity also are common in the recovery boiler steam/water cycle. A detailed discussion of the various analytical test procedures is beyond the scope of this presentation. Volumes 11.01 and 11.02 from the American Society for Testing and Materials (ASTM) are good resources for both grab sample and on-line standard test methods.

Specific Conductivity

Some of these parameters were already defined in the online analyzer section. Key aspects of Specific Conductivity are summarized in Figures 13 and 14.

Figure 13 - Specific Conductivity Introduction

- Total Conductive Solids (Salts, Acids, Alkalis)
- High Levels Can Cause Foaming and/or Corrosion
- Units: Usually µS/cm
- Micromho (µmho/cm) = Microsiemen (µS/cm)
- Millimho (mmho/cm) = Millisiemen (mS/cm)
- 1 mS/cm = 1000 µS/cm (Beware of auto-switching ranges on meter!)

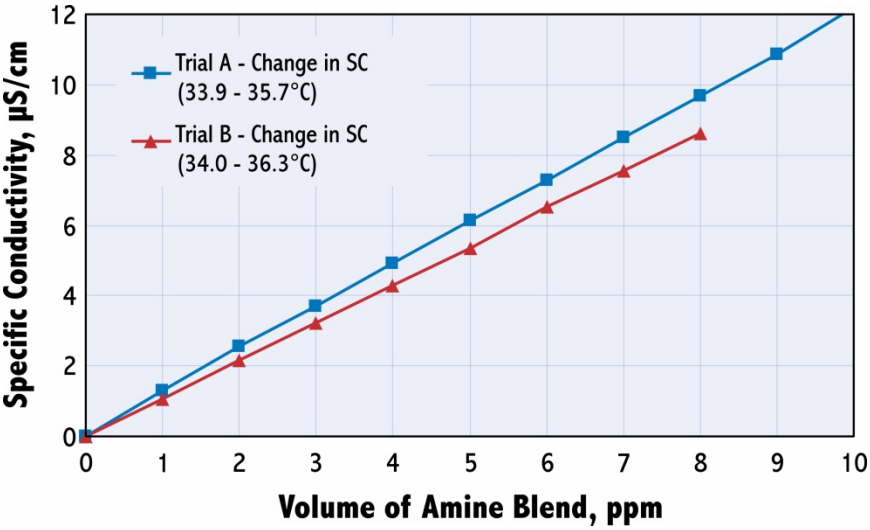
Figure 14 - Specific Conductivity - Typical Values

Sample	Normal Values µS/cm	Main Source
Demineralized Water	0·055-5·0	NaOH Leakage - Ion Exchange CO_2 - RO Units
Condensate & Feedwater	2·0-6·0	Neutralizing Amine Feed
Boiler Water	20-150(a)	3 to 5 × ppm PO_4

(a) Much higher for low pressure boilers on softened makeup

Figure 15 presents an example of the effect of a neutralizing amine blend used at one pulp and paper mill on the specific conductivity of a sample of demineralized water. Because the demineralized water used contained some background conductivity, the change (rather than the actual value) in specific conductivity was plotted versus concentration. The effect is quite linear - although slightly different rates of change can be obtained depending on laboratory technique.

Figure 15 - Neutralizing Amine Effect on Conductivity (Example)



pH

Figure 16 presents the pH scale described earlier for online analyzers. The graphic shows that each pH unit corresponds to a 10-fold change in the concentration of alkali or acid. Demineralized water pH values are difficult to measure because they are roughly neutral (pH 7) and any contamination can cause a significant change. Condensate and feedwater have mildly alkaline pH values (pH 9) from the addition of amine and boiler water has alkaline pH values (pH 10) from sodium phosphate and caustic addition.

All pH limits are based at 25°C, and samples should be at this temperature - as pH readings typically decrease by 0.3-0.4 units per 10°C increase in temperature.

Figure 16 - pH (Relative Acidity and Alkalinity)

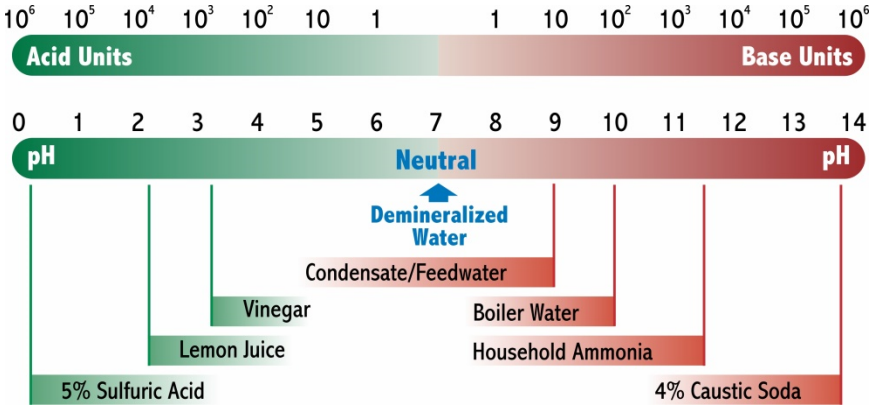


Figure 17 shows the effect of the amine blend tested in Figure 15 on the pH values of a sample of slightly alkaline demineralized water. The greatest change in pH values was noted up to about a pH of about 9.0-9.1 or about 4.5-5.5 ppm of the amine blend. Thereafter, the rate of pH increase decreases substantially. It is this leveling in the pH with higher amine levels which makes pH less useful for detecting an overfeed of amine. Specific conductivities usually provide a better indication of total amine in the condensate, feedwater and steam. Since the sample temperatures (~35°C) during this testing were high by 10°C, actual pH values (at 25°C) would have been about 0.3 pH units higher than the values shown in Figure 15 (i.e., pH of 9.3-9.4 for 4.5-5.5 ppm of the amine formulation). The particular amine blend is believed to contain less than 50% water.

Figure 17 - Example of Amine Blend Effect on pH

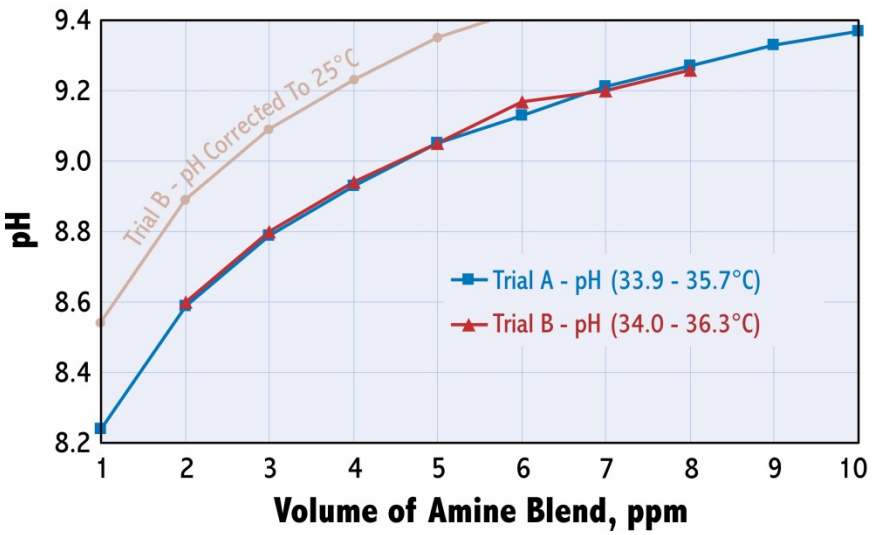


Figure 18 shows the general trend of iron oxide transport with increasing feedwater pH from ammonia. Similar trends have been noted with blends of neutralizing amines. Figure 19 shows the changes in corrosion product transport for two copper alloys exposed to condensate containing ammonia (7). Minimum copper transport for these data occurred around a pH of 8.5-9.2. Other studies have shown a minimum copper transport rate in a reducing environment may occur at slightly higher pH values. Condensate and feedwater pH control ranges represent a compromise between minimizing copper and steel corrosion rates. Some mills with minor amounts of copper heat exchangers favor high pH ranges (9.2-9.4) to minimize iron oxide transport. Lower pH (8.5-9.0) and amine levels are sometimes selected in pulp mills to lower the background conductivity from amines and thereby increase the ability to detect and eliminate intrusion of corrosive and deposit forming contamination. A pH target of about 9 probably is most common for condensate and feedwater.

Figure 18 - Effect of pH on Feedwater Iron Transport

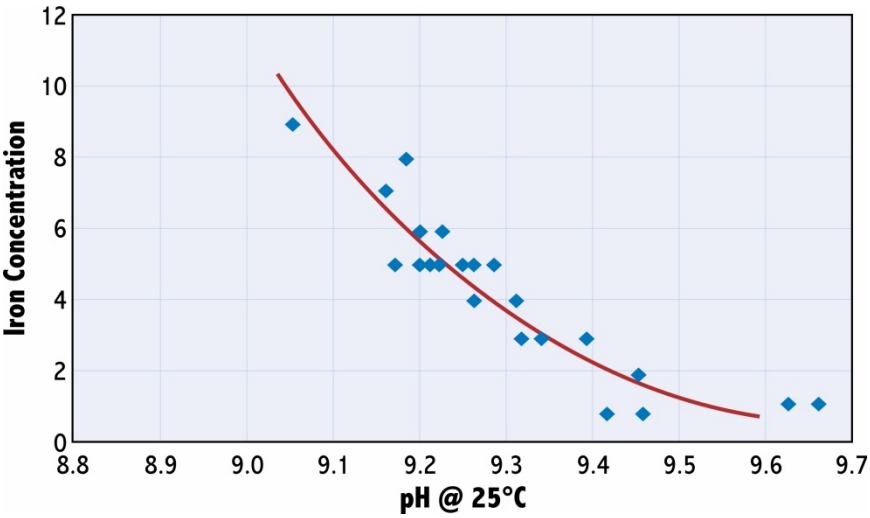


Figure 19 - Effect of pH on Copper Transport

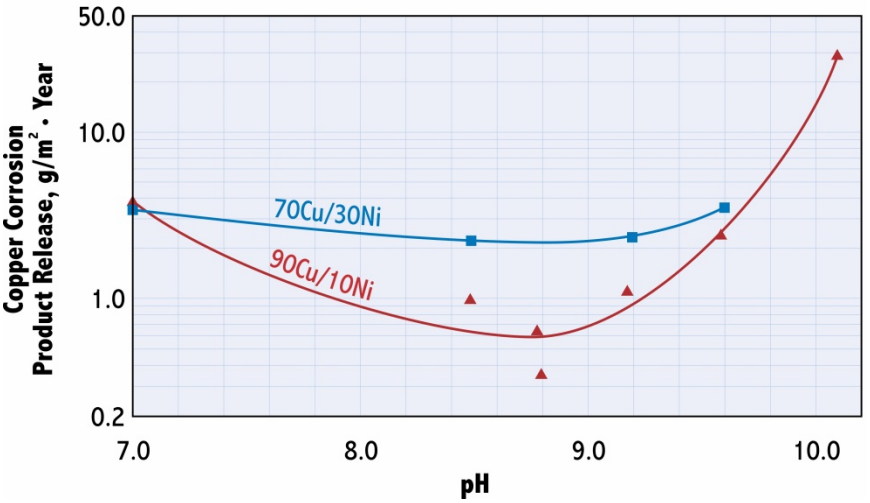


Figure 20 shows the effect of pH on the corrosion of iron in the boiler water (8).

Figure 20 - Effect of pH on Steel Corrosion in Boiler

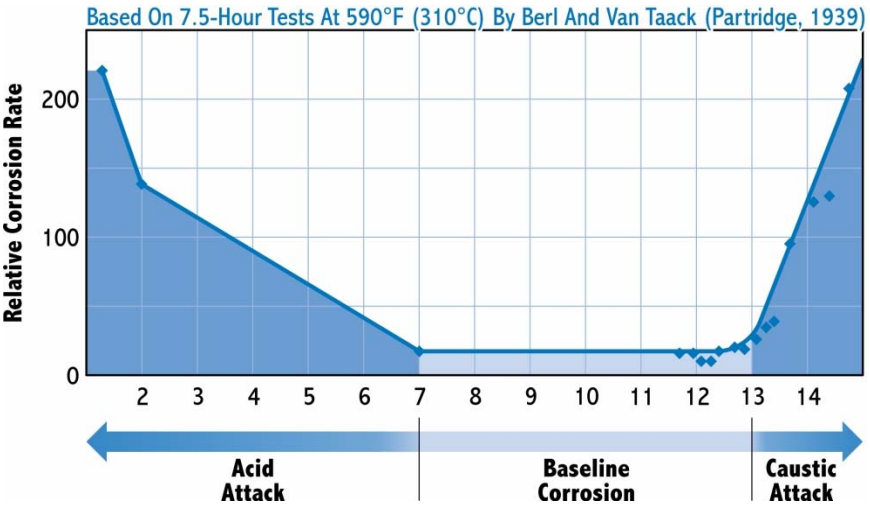
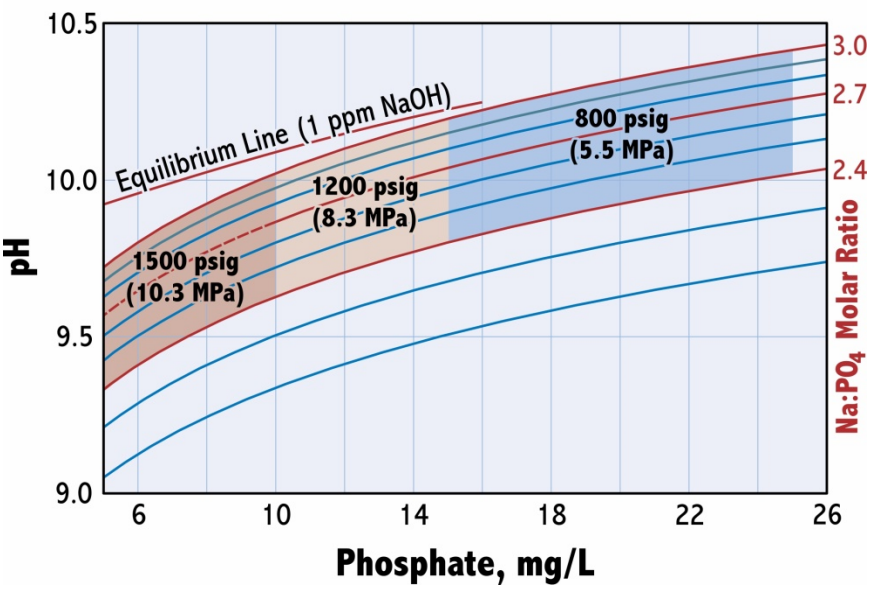


Figure 21 shows the basic control ranges for phosphate treatment for 800 to 1500 psig boilers.

Figure 21 - Phosphate/pH Control Curves

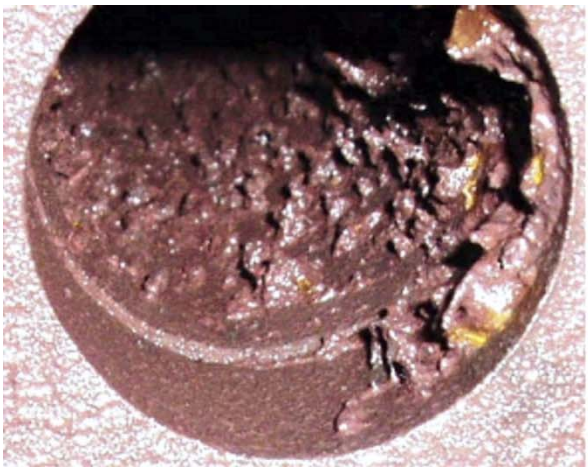


Dissolved Oxygen and Oxygen Scavengers

The third parameter which needs to be understood and monitored is the level of dissolved oxygen. Dissolved oxygen corrodes copper and can cause pitting of steel.

Figure 22 shows a picture of in-service oxygen attack of a carbon steel economizer tube as it exits an economizer inlet header in a black liquor recovery boiler with softened makeup. This resulted from a combination of poor deaerator performance and air inleakage across the boiler feed pump. Dissolved oxygen also contributes to corrosion fatigue and stress assisted corrosion in economizers.

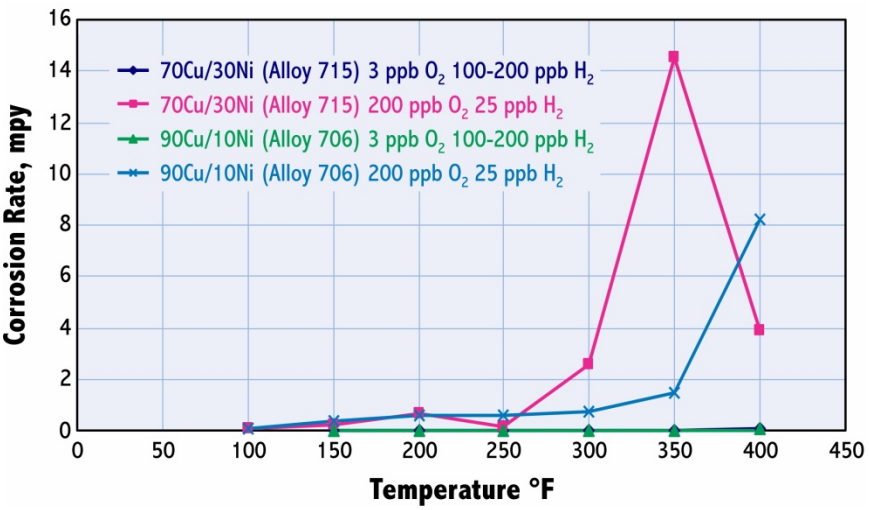
Figure 22 - Dissolved Oxygen



- Oxygen as O_2 (from air) dissolved in water.
- Excessive DO & High Conductivity Pits Steel.
- Contributes to Corrosion Fatigue & SAC.
- #1 Corrodes Copper.

Figure 23 shows the combined effect of elevated temperatures and dissolved oxygen on two copper nickel alloys. Plain copper alloys would be expected to corrode to a greater extent and at lower temperatures than indicated for copper nickel.

Figure 23 - Dissolved Oxygen Effect on Copper Corrosion



Normal values and sources of dissolved oxygen in mill water condensate and feedwater are summarized in Figure 24. Raw and demineralized water generally is saturated with dissolved oxygen, which corresponds to a tremendous amount of dissolved oxygen (8,000-14,000 ppb) at ambient temperatures. Considering that the target is <5-10 ppb of dissolved oxygen, only 0.1% (below level detected by conductivity) intrusion of raw or mill water into condensate can cause high dissolved oxygen. The most important mantra for dissolved oxygen control is "where water or steam leaks out, air leaks in". Controlling dissolved oxygen requires constant monitoring to detect and minimize air leakage via steam and water leaks.

Figure 24 - Dissolved Oxygen

Normal Values

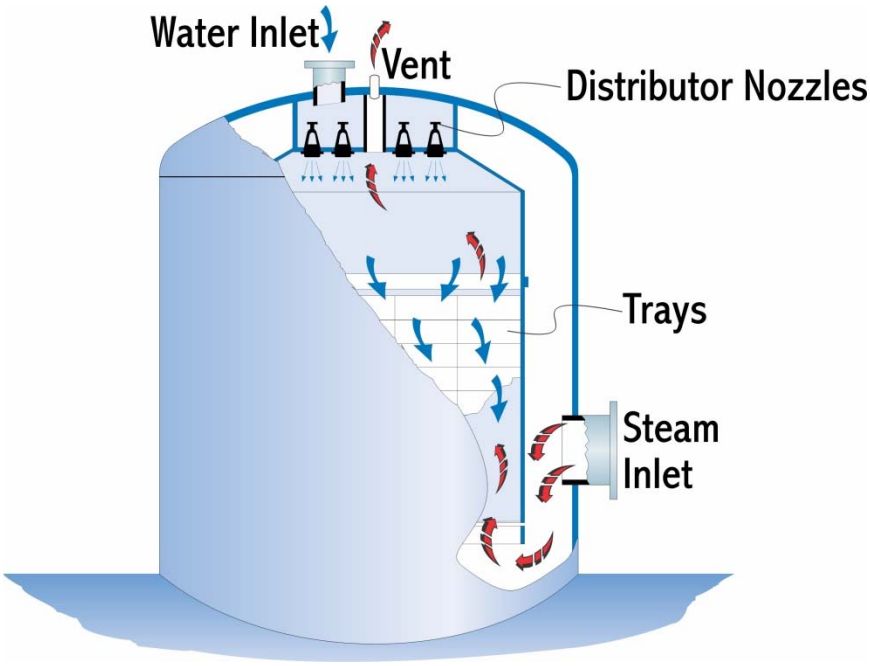
- Mill Water or Demineralized Water: 8,000 - 14,000 ppb
- Condensate: 10 - 100 ppb O_2
- Feedwater: <5 - 10 ppb O_2 (ASME Limit <7 ppb)

Sources

- Air Leaks: Where Water Leaks Out, Air Leaks In
- 0.1% Mill Water = 8 - 14 ppb O_2

The main means of removing oxygen from water is through the mechanical removal of oxygen in a deaerator. A simplified diagram is presented in Figure 25.

Figure 25 - Dissolved Oxygen Control: Deaerator



This is a direct contact steam heater with countercurrent flow of steam and water. Modern deaerators have spray and tray sections to effect oxygen removal. It functions by spraying the water into fine droplets, heating water to the boiling point (where the solubility of oxygen in water is negligible), and stripping the residual oxygen and other noncondensable gases out with a small counter-current flow of steam. Figure 26 shows a photograph of the spray nozzles for a medium size deaerator. Figure 27 shows a photograph of the trays below the spray nozzles.

Figure 26 - Deaerator Spray Nozzles Photograph

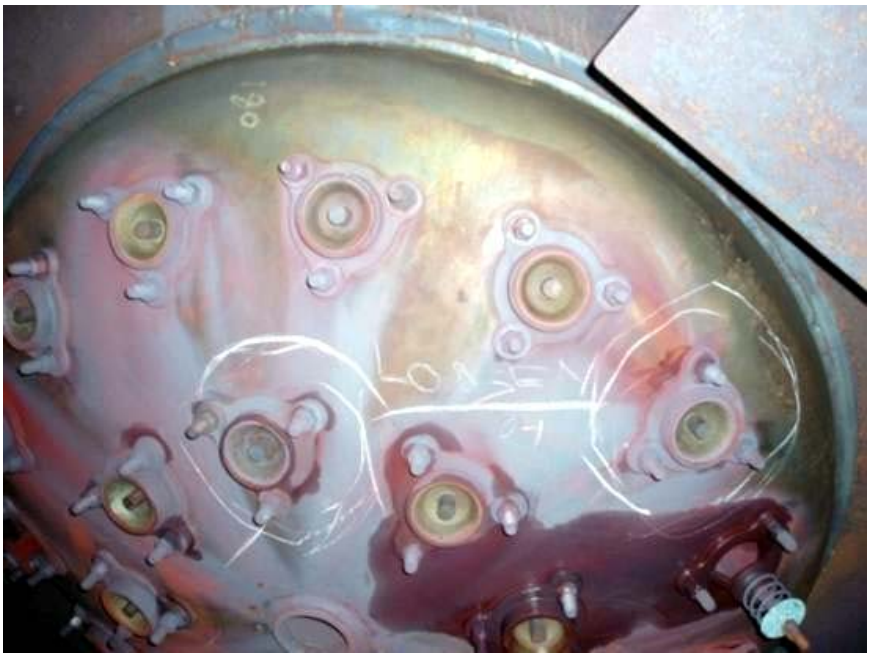


Figure 27 - Deaerator Trays Photograph



The deaerator should remove dissolved oxygen levels down to <5-10 ppb. To achieve the dissolved oxygen levels for optimal control of copper corrosion in the condensate system, an oxygen scavenger is applied. While low pressure boilers on softened makeup often use the best oxygen scavenger (sodium sulfite), sodium sulfite adds solids to the boiler water and often decreases the condensate pH for high pressure boilers. Therefore, volatile reducing agents are usually applied as oxygen scavengers to modern recovery boilers.

The most common volatile oxygen scavenger since about the mid 1950's was hydrazine. However, due to suspect carcinogenicity of hydrazine, a variety of organic substitutes were developed and are more common in the pulp and paper industry. For cycles containing copper, hydrazine often still is the preferred oxygen scavenger by power industry chemists due to the lack of harmful decomposition products.

Carbohydrazide is considered to be the closest equivalent to hydrazine and may actually be more effective in low temperature systems. As indicated in Figure 28, carbohydrazide reacts directly with oxygen and excess carbohydrazide decomposes to hydrazine and carbon dioxide (or carbonic acid in water). The other hydrazine substitutes generally result in more decomposition products and are thus considered to be less desirable. While originally patented, the patent on carbohydrazide has run out and the chemical now is available from numerous vendors. In addition to the scavenging reaction, carbohydrazide and other scavengers function as reducing agents which convert red rust (hematite) to black rust (magnetite).

Figure 28 - Oxygen Scavengers – Carbohydrazide Example

- Oxygen Scavenging (Reduces Oxygen)
  - Oxygen + Carbohydrazide → Inerts + Carbonic Acid
- Passivation
  - Red Rust + Scavenger → Black Rust + Carbonic Acid

In some mills, the deaerator works very well at mechanically removing oxygen and dissolved oxygen is only occasionally tested as part of deaerator performance testing. In such an event, the oxygen scavenger would be monitored on a routine basis in the feedwater. Some facilities monitor both, which is preferred. Very low dissolved oxygen levels (<2 ppb), excessive velocities (or two-phase flow), and excessive feed of oxygen scavengers can lead to flow accelerated corrosion of carbon steel feedwater lines. Therefore, the excess of oxygen scavenger should be limited by monitoring the residual and/or carefully regulating the feed rate. A summary of the concerns with underfeed or overfeed of carbohydrazide and other oxygen scavengers is presented in Figure 29.

Figure 29 - Oxygen Scavenger Feed

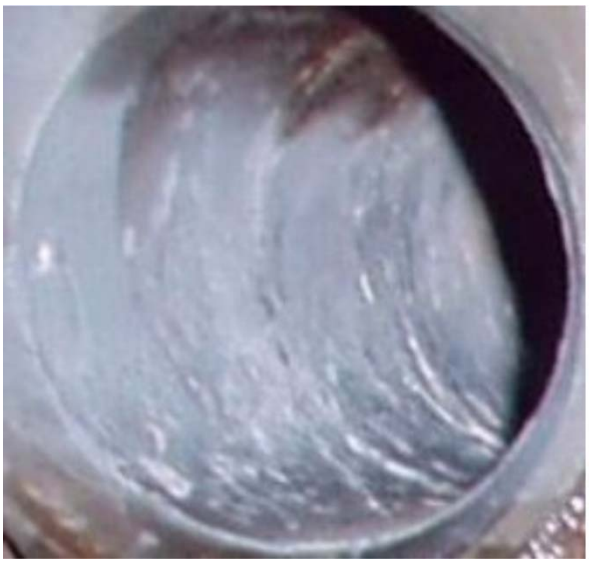
- Overfeed
  - FAC: Flow Accelerated Corrosion and Rupture of Steel Pipe Lines (e.g., Feedwater Line)
  - Decomposition Products
- Underfeed
  - Copper Corrosion in Steam/Condensate System
  - Pitting of Economizer
  - Corrosion Fatigue of Economizers

For facilities requiring the equivalent of 20-40 ppb of hydrazine (28-56 ppb carbohydrazide) or more, monitoring for flow accelerated corrosion (FAC) of feedwater system components during scheduled outages is recommended. Feedwater line failures from FAC have resulted in fatalities in the power industry.

Hardness

Figure 30 shows a picture of hardness phosphate deposit in a black liquor recovery boiler generation bank tube. Hardness is soluble in water at room temperature and it precipitates at the high temperatures and high pH values present in the boiler.

Figure 30 - Hardness in Generation Bank Tube



- Hardness scale in generation bank tube, dispersant treatment.
- Without dispersants, gray mayonnaise deposits are in drums.

As indicated in Figure 31, it precipitates as hardness phosphate for boilers on phosphate treatment. If the phosphate is depleted, acid can be produced by the liberation of free sulfates or chlorides. Similarly, precipitation associated with alkalinity compounds (not shown) from the water can result in the production of caustic. Acid production will predominate if alkalinity in the mill water is less than the combined chloride and sulfate present. This is fairly common for pulp and paper mill water as a result of alum addition (which adds sulfate and lowers alkalinity) during clarification.

Figure 31 - Hardness Definition

- Mainly the Calcium (Ca) and Magnesium (Mg)
- Precipitates and Forms Hardness Scale In Boiler
- Precipitation Can Result in Decreased Boiler pH

$$\text{Hardness} + \text{Phosphate} \rightarrow \text{Sludge} + \text{Salt} + \text{Acid}$$

$$\text{Calcium Sulfate} + \text{Sodium Phosphate} \rightarrow \text{Calcium Phosphate} + \text{Sodium Sulfate} + \text{Sulfuric Acid}$$

$$3CaSO_4 + 2Na_2HPO_4 \rightarrow Ca_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4$$

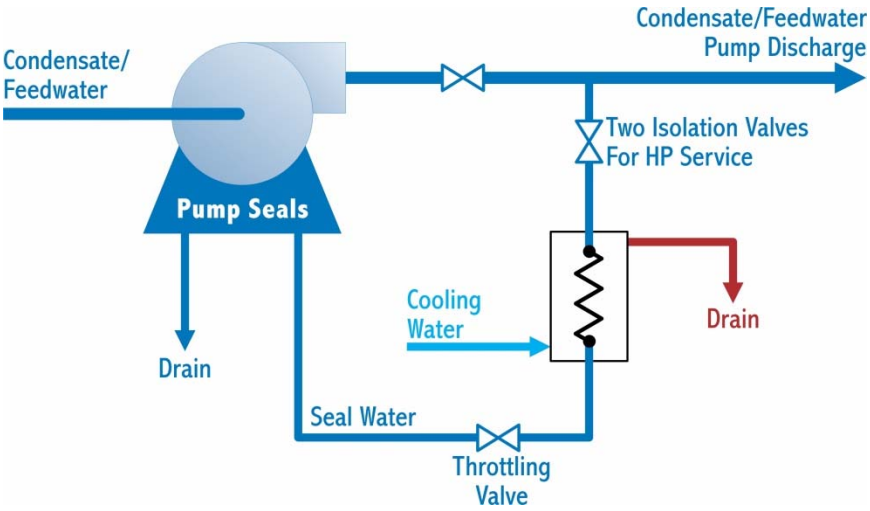
Essentially boilers have a zero tolerance for hardness in the feedwater in the absence of dispersants or chelants. For lower pressure boilers, dispersants usually are applied to minimize deposition. The ASME consensus guidelines indicate more liberal hardness limits than indicated in Figure 32 (9). Boilers on softened makeup sometimes can tolerate higher levels of hardness.

Figure 32 - Hardness Limits

- Expected Values
  - ASME Limits: <0.2 451-750 psi, < 0.1 mg/L 751-900 psi, <0.05 mg/L 901-1000 psi, >1000 psi (NONE)
- Detection Limits:
  - ~0.1 mg/L titration methods
  - <0.02-0.05 mg/L spectrophotometric methods (some cite lower)
- Sources
  - Mill Water In Condensate/Feedwater
  - Problem In Makeup Demineralization System
- Controls
  - Dump Valves to Sewer Condensate
  - Condensate Polishers (Softeners) To Remove Hardness

The main sources of hardness are mill water via seal water leaks and leaky heat exchangers and problems with the makeup plant. The main controls are just limiting the sources, dumping contaminated condensate, and polishing traces of hardness contamination in a softener. Figure 33 presents an example of a seal water retrofit which has been implemented at numerous facilities to eliminate a source of hardness contamination.

Figure 33 - Control of Hardness: Prevent Intrusion



Phosphate

The reasons for phosphate testing and phosphate treatment are summarized in Figure 34.

Figure 34 - Purpose of Phosphate (PO_4) Treatment

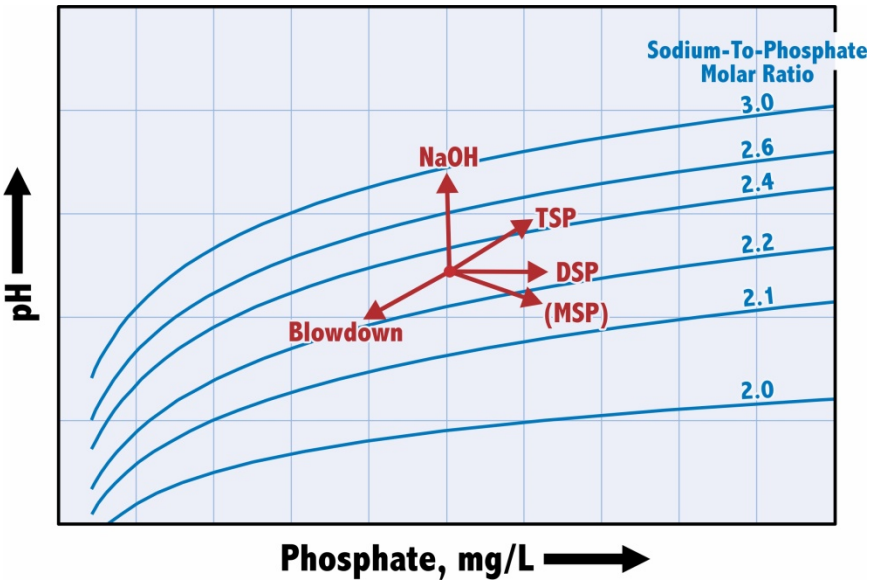
- Stabilizes pH
- Precipitates Hardness as Softer Deposits
- Backup Indication of Hardness Contamination

Figure 35 shows the effect of trisodium phosphate (TSP), disodium phosphate (DSP), monosodium phosphate (MSP), and sodium hydroxide (NaOH) additions and boiler blowdown on pH and phosphate levels. For stable boiler chemistry, boiler blowdown rates should normally be fixed.

Some mills are using more stringent phosphate control ranges than indicated in the curves. In the absence of feedwater contamination, lower phosphate levels generally results in a cleaner boiler. However, lower phosphate levels require better control of feedwater purity and better online monitoring to detect chemistry upsets. Therefore, the higher ranges presented here are often used in older mills.

Polymers also are commonly used for boiler water treatment in pulp and paper mill boilers as deposit control agents. Formulations applied are usually proprietary and limits associated with their use are usually vendor specific.

Figure 35 - Phosphate Effect on Boiler Water pH



SUMMARY OF STEAM/WATER CYCLE CHEMISTRY

Figure 36 provides a summary of the material covered in this presentation. Familiarity with some fundamental chemistry parameters provides the basis for subsequent control of chemistry in the recovery boiler and the remainder of the steam/water cycle. Control of deposition on the waterside surface of boiler tubes is the primary purpose of treatment since this material contributes to both overheating and waterside and fireside corrosion. Most of these deposits are corrosion products transported into the boiler with the feedwater or are due to makeup or condensate contamination. Controlling the ingress of these materials requires proper makeup water, condensate, and boiler water treatment and chemistry monitoring and control. We also briefly mentioned the need to control steam silica and sodium avoid steam turbine deposits.

Figure 36 - Summary: What Should You Know Today?

- What Can Go Wrong and Goals (Control Deposition & Corrosion)
- Steam/Water Cycle, Basic Components
- Top Chemistry Parameters to Protect Recovery Boilers
  - Conductivity µS/cm
  - pH
  - Dissolved Oxygen, ppb O_2 (and Oxygen Scavengers)
  - Hardness, ppm $CaCO_3$
  - Phosphate, ppm PO_4
- Other Parameters Mentioned
  - Protect Turbines: <10 ppb as Na of Sodium and < 20 ppb as SiO_2 of Silica
  - Feedwater Corrosion Products: Iron (Fe) and Copper (Cu)

This presentation provided a brief introduction to a small portion of recovery boiler water treatment. Recovery boiler water treatment requires an understanding of much more than the boiler water sample chemistry. One needs to have an understanding on all facets of the steam/water cycle. As indicated in Figure 37, to properly provide training on these topics would require more detail on the areas covered as well as additional training modules.

Figure 37 - Additional Steam/Water Cycle Chemistry Topics

- Makeup Water Treatment
- Condensate Collection and Treatment
- Feedwater Treatment System
- Boiler Water Treatment
- Steam Purity Considerations
- Additional Chemistry Testing
- Preventive Maintenance
- Personnel Training
- Chemical Cleaning

Treatment starts with makeup water which should be demineralized following whatever pretreatment is necessary to protect the demineralization equipment and to make the process more efficient. All piping and vessels exposed to mixtures containing demineralized water upstream of the deaerator should be lined (as in the case of the demineralizers) or constructed of stainless steel to minimize corrosion and corrosion product transport to the boiler. Condensate should be polished to remove suspended matter and dissolved contaminants. Oxygen scavenging and pH control chemicals are usually added to the feedwater to minimize corrosion.

After feedwater enters the boiler, a treatment appropriate to the operating conditions of the boiler is used. This is most frequently phosphate-based, although other boiler water treatment programs also are discussed. Emergency response procedures for boiler water treatment programs also are presented. Blowdown and proper operation of the boiler minimize carryover.

The steam/water cycle should be equipped with sufficient instrumentation to provide on-line monitoring of most critical chemistry parameters. Grab sample monitoring should be performed routinely to supplement the on-line monitoring data and to provide checks of on-line analyzer performance. Equipment must be maintained through

preventive maintenance programs, and personnel must be trained. Last, but not least, boilers usually will require occasional chemical cleaning to reestablish clean boiler tube surfaces.

Relevant TAPPI Guidelines

Figure 38 lists TAPPI guidelines prepared by Technical Committees of TAPPI relating to steam/water cycle treatment programs. These are included in a large collection of "TIPS" from TAPPI (www.tappi.org) or each TIP can be obtained individually for a nominal charge (3, 10-15).

Portions of these documents were referenced and discussed during this presentation. These references are good sources of information. They are periodically reviewed and edited by a TAPPI water treatment committee.

Figure 38 - For More Information

- TAPPI Technical Information Papers
  - TIP 0416-03 – Water Quality and Monitoring Requirements for Paper Mill Boilers Operating on High Purity Water
  - TIP 0416-04 – Design Engineer Decision Tree: Paper Mill Boiler Feedwater
  - TIP 0416-05 – Response to Contamination of High Purity Boiler Feedwater
  - TIP 0416-06 – Keys to Successful Chemical Cleaning of Boilers
  - TIP 0416-07 - Evaluating Reverse Osmosis for Treating Makeup to the Boiler Feedwater in a Pulp and Paper Mill
  - TIP 0416-13 - Water Treatment-related Opportunities for Energy Conservation in a Paper Mill Powerhouse
  - TIP 0416-14 - Water Quality and Monitoring Requirements for Paper Mill Boilers Operating with Softened Makeup Water
  - BLRBAC - Boiler Water Management Guidelines for Black Liquor Recovery Boilers, April 2016.

As of November 2011, the Black Liquor Recovery Boiler Advisory Committee (BLRBAC) was working on five documents relating to water treatment. None of the documents had been promulgated when this presentation was prepared, but it is expected that BLRBAC may be another source of information in the future.

Many of the recommendations in these chemistry guidelines and discussed in today's presentation involve equipment for treating water rather than just the chemicals added. I would like to leave the reader with the following principle. Often the best solution to a chemical problem is a mechanical one. Chemical treatment should be a supplement to a well-designed system, not a bandage for a broken one.

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13. TAPPI, Evaluating Reverse Osmosis for Treating Makeup to the Boiler Feedwater in a Pulp and Paper Mill, TIP 0416-07.
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15. TAPPI, Water Quality and Monitoring Requirements for Paper Mill Boilers Operating with Softened Makeup Water, TIP 0416-14
16. BLRBAC, Boiler Water Management Guidelines for Black Liquor Recovery Boilers, April 2016.