RECOVERY BOILER WATER TREATMENT

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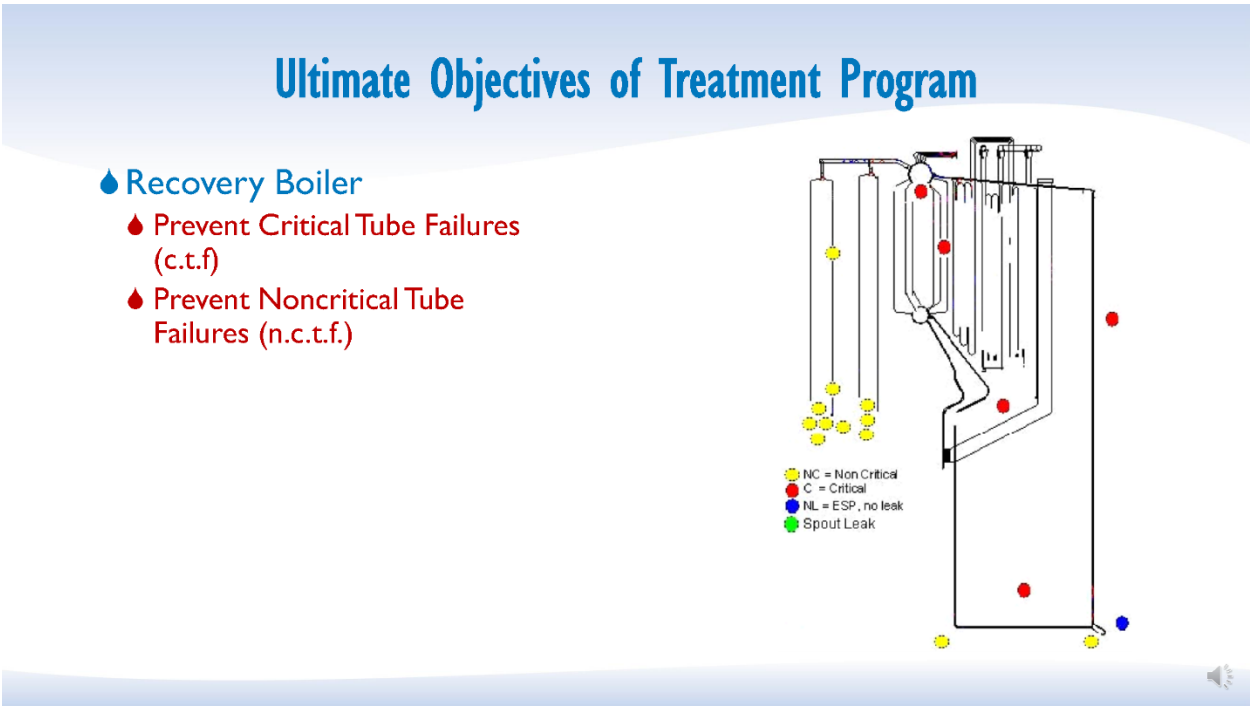
INTRODUCTION

This presentation provides an introduction to Recovery Boiler Water Treatment. The goals of the course are to become familiar with the objectives of recovery boiler water treatment and the basic components of the steam/water cycle, understand the effects of deposits on the boiler, and be familiar with routine chemistry monitoring.



The ultimate objective of the treatment program is preventing critical tube failures in the recovery boiler. Critical tube failures are failures in which water leaks from the boiler into the primary furnace and contacts the smelt bed. The water and smelt react generating a shock wave that can blow the boiler apart. Each red circle represents an example of a critical tube failure which occurred in 2018 (reported at the fall 2018 Black Liquor Recovery Boiler Advisory Committee meeting). Critical tube failures can include floor tubes, waterwall tubes, screen tubes and

generation bank tubes. There are also noncritical tube failures which are shown by the yellow circles. These failures are mainly in the economizer or outside of the boiler and they are not likely to reach the smelt bed or result in a smelt/water reaction.



The treatment program should be designed to also protect the rest of the steam/water cycle. This includes avoiding deposition on steam turbines by keeping the steam sodium less than 10-20 ppb (as Na) and steam silica less than 20 ppb (as SiO_2). The photograph shows an example of excessive sodium salts deposited on a high pressure (HP) steam turbine which can reduce capacity and efficiency. In some cases, turbine deposits can contribute to corrosion or cracking. In the back of this photograph, one can see the larger, longer LP turbine blades. Silica is semivolatile in that it is volatilized (evaporated) from the boiler and deposits mainly in the low pressure (LP) end of the turbine. Silica deposits are not corrosive, and a greater volume of deposition is needed in the LP turbine before you would expect to experience a load reduction.

The steam water cycle also includes a lot of copper and copper alloy tubes in heaters and condensers and long networks of carbon steel piping. The chemistry program should protect surfaces from damage, such as that shown here, and reduce corrosion product transport from this equipment to the boiler. Portions of some condensate system now may include stainless steel piping, which generally should introduce little to no corrosion product transport.



This figure presents a simplified recovery boiler steam/water cycle diagram. The blue lines are water. The red lines are steam. The black circles with an "S" are sample points, the pink circles are online analyzers. There are usually samples before and after each component to diagnose problems.

The cycle starts with treated makeup water flowing into the system. For modern recovery boilers the makeup is demineralized, and the specific conductivity is continuously monitored. As shown, it is recommended to have an automatic block and dump system so that if the makeup is contaminated, it is isolated, and the Mill can operate on clean makeup from the storage tank until the treated makeup problem is resolved. The makeup usually flows through heat recovery heat exchangers and there should be a sample after each heat exchanger to troubleshoot contamination incidents.

Following heat recovery, the makeup flows to the deaerator, which removes air from the makeup and condensate. After deaeration, amines and oxygen scavengers are applied to the heater drop leg, storage tank or storage tank drop leg. Dissolved oxygen is monitored either before or after the boiler feed pump. The feedwater may flow through a feedwater heater and then into the boiler.

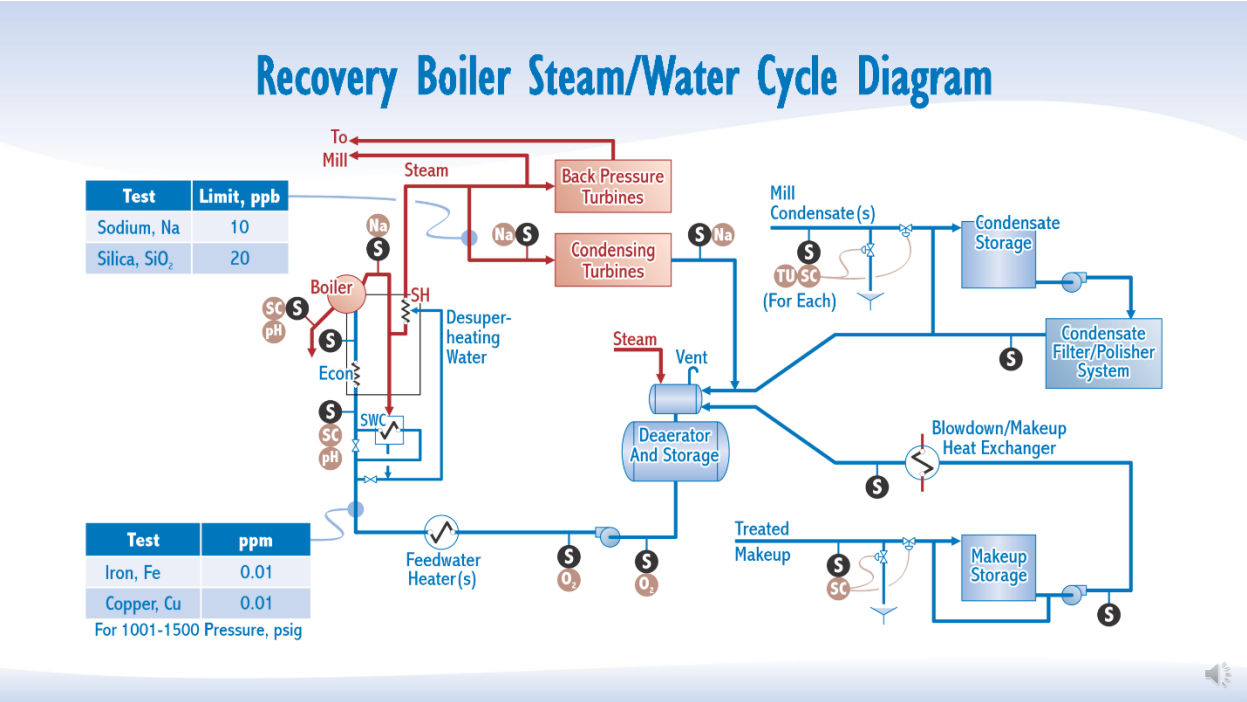
The feedwater flows through economizers and then into the steam drum, where it mixes with boiler water. The boiler water flows down the downcomers, through the steam generation tubes and the steam is separated from boiler water in the steam drum. There is a continuous blowdown of boiler water from the steam drum which is continuously monitored for pH and specific conductivity.

Saturated steam leaves the steam drum and flows through a series of superheaters, usually with intermediate water injection for desuperheating. The superheated steam is shown supplying a condensing steam turbine, where continuous steam sodium monitoring is standard. This is shown having nominal steam purity limits of 10 ppb sodium and 20 ppb silica, although some turbines may have more stringent limits. The sodium can come from two sources, from mechanical carryover of boiler water and from attemperation water. Most modern recovery boilers normally have a sweetwater condenser, which condenses saturated steam and uses the condensed steam for attemperation. However, as shown in the figure, there usually is a backup system of direct feedwater attemperation resulting in feedwater contamination bypassing directly into the steam.

Steam is supplied to the mill primarily through backpressure turbines. After use, the mill steam is condensed and collected in separate condensate collection tanks for evaporators, liquor heaters, digesters, glycol heaters, etc.. Each tank has conductivity monitoring and dump system setup to detect and prevent that process contamination from returning to the cycle. Most of the condensates are then combined together and passed through a condensate polishing and filtration system. There are several types of condensate polishers. Cation exchange softeners usually regenerated with amines are the most common. Mixed bed polishers also may be used to demineralize the condensate – particularly in cycles 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 beds also can leak carbon fines. The polished condensate is returned to the deaerator which completes the steam/water cycle.

Condensates normally expected to be clean, such as turbine condensate may return directly to the deaerator. As shown, sodium monitoring often is an effective way to detect trace condenser tube leakage. Other streams such as air heater condensate should have sample points for use during upsets such as when a black liquor steam-out line flowed backward and contaminated the low-pressure steam feeding the air heaters with liquor.

Large amounts of iron and copper can be returned with the condensate, and we have shown the ASME feedwater limits of 0.01 ppm for iron and copper for >1000 psig boilers. Boiler tube deposits normally consist mainly of iron and copper oxides from the feedwater and their concentrations in condensate and feedwater should be minimized.



The chemistry objectives of the treatment program are to prevent deposition and corrosion. In the condensate and feedwater systems, no deposition is expected, but at least a minor amount of corrosion is expected.

Corrosion products in the feedwater can deposit in the economizer, but the heat flux is usually low, and deposition is of minor consequence. The economizer also can experience localized damage from corrosion fatigue (CF) and stress assisted corrosion (SAC), but the expectation is of little or no corrosion.

Waterwall tubes will accumulate deposits. The solubility of iron and copper decreases as the temperature increases resulting in deposition. If hot side tube deposits exceed 20-25 g/ft^2 of deposit, you should consider chemically

cleaning the boiler to remove the deposition. As long as you control boiler chemistry and limit waterwall tube deposits, waterwall tubes should experience negligible or minor amounts of internal corrosion over the life of the boiler.

Superheaters and turbines are not expected to experience detectable deposition or corrosion. There is scale that forms in superheater tubes from steam oxidizing steel surfaces, but that will occur regardless of chemistry control and so is not considered deposition or corrosion related to the treatment program.

Chemistry Objectives of Treatment Program

Component	Deposition	Corrosion
Condensate System	--	Minor
Feedwater System	--	Minor
Economizer (n.c.t.f.)	Minor	0 or Minor
Waterwalls (c.t.f.)	≤20-25 g/ft^2	0 or Minor
Superheaters	0	0
Turbines	0	0

n.c.t.f = noncritical tube failures; c.t.f = critical tube failures

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The tube in this figure is a waterwall (nose) tube about 3 inches in diameter with about a ¼-inch thick tube wall. Suspended corrosion products and other materials entering the boiler with the feedwater mix with boiler water, flow down the downcomers, and flow up this and other waterwall tubes. As shown in the figure, these materials deposit on the hot side of the tube. These deposits consisted mainly of iron, copper, and carbon.

The heat flowing through the tube wall backs up behind the thick, insulating deposits resulting in higher tube metal temperatures. The boiler water flowing up this tube also is flowing through the porous deposit layers to the tube metal surface. Boiler water reaching the tube metal surface absorbs heat and generates steam. The deposits restrict the water flow which inhibits cooling, and the tube metal gets hotter. What happens when that tube gets hot?

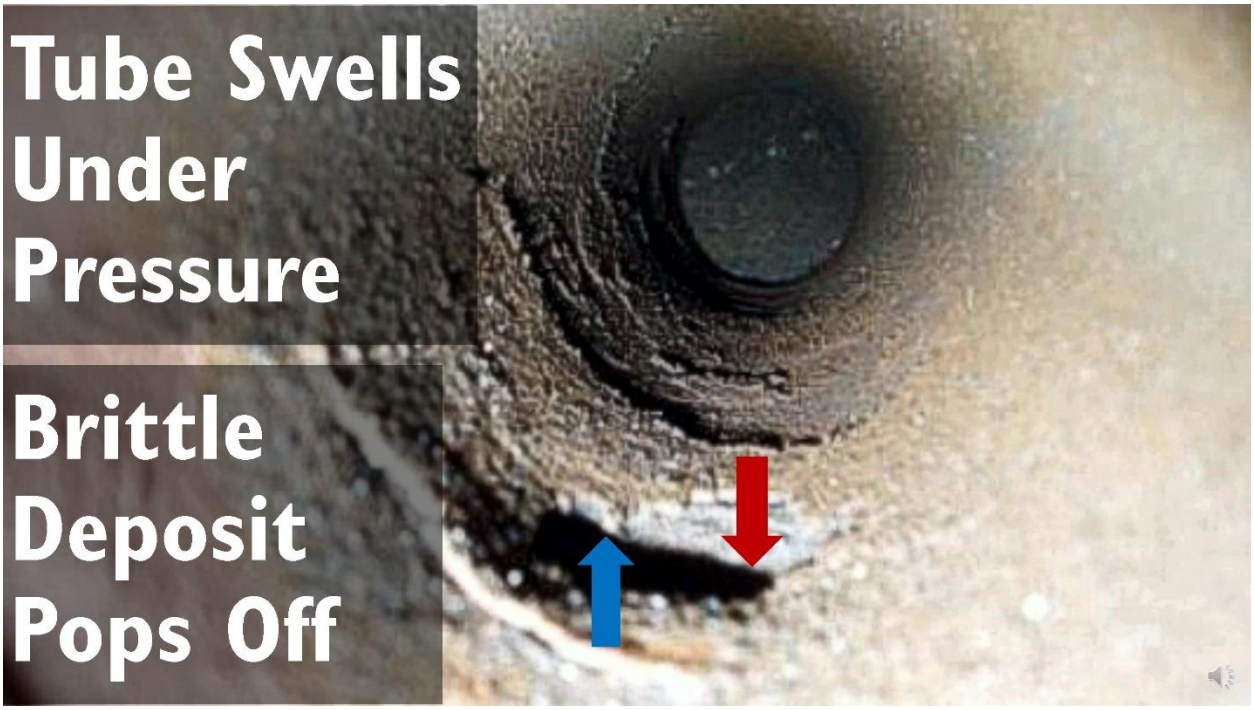


When a black smith pulls a piece of very hot steel out of the fire, a simple hit of the hammer can flatten the metal because when metal gets hot it gets soft.



This figure provides an end-view of the interior of a waterwall tube. When deposits prevent proper cooling of a waterwall tube, the tube temperature rises, loses its strength and the internal pressure will cause the tube to swell like a balloon under deposits. The deposit is brittle, so it pops off and allows the boiler water to rush in and quench the

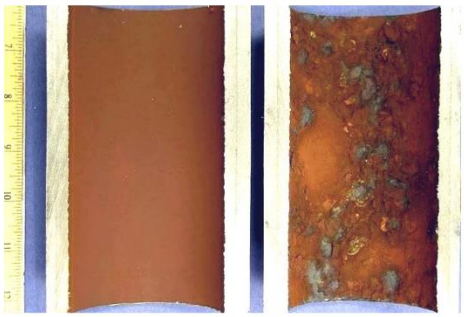
tube metal. That restores the strength of the steel and can stop tube expansion. If you are lucky, you are left with a bulge or a blistered tube, but this also can lead to rapid, large tube failures.



The picture at the right shows a top view of a boiler tube that expanded from heavy waterside deposits. In addition to overheating and bulging, this tube experienced underdeposit corrosion and hydrogen damage. The picture on the left shows the waterside surfaces of a tube sample that was split vertically along the membrane between the hot and cold sides. The cold side is on the left and has a thin film of deposit but no corrosion and is in excellent condition. When the boiler was new and clean, the hot side looked just like the cold side. Following years of operation, the hotside, which is on the right had heavy deposits and underdeposit corrosion. Fireside corrosion also can cause fireside corrosion.

Common Chemistry-Related Waterwall Tube Failures

- Overheating due to Heavy Waterside Deposits
- Underdeposit Waterside Corrosion
- Fireside Corrosion from Heavy ID Deposits



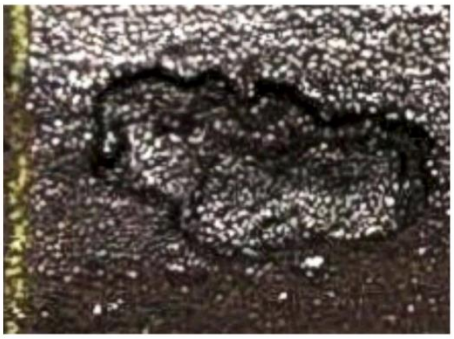


The photograph on the left shows a close-up view of a patch of adherent deposit on waterside surfaces following brushing to remove loosely adherent material. When the adherent deposits were removed, a deep gouge was visible underneath. This tube experienced underdeposit corrosion. Note that the metal around the deposit plug was intact with essentially no corrosion. Thus, underdeposit corrosion requires both heating and deposition.

Recovery Boiler Waterside Corrosion Example



- Localized Patch of Waterside Deposit after Brushing Off Loose Surface Deposits

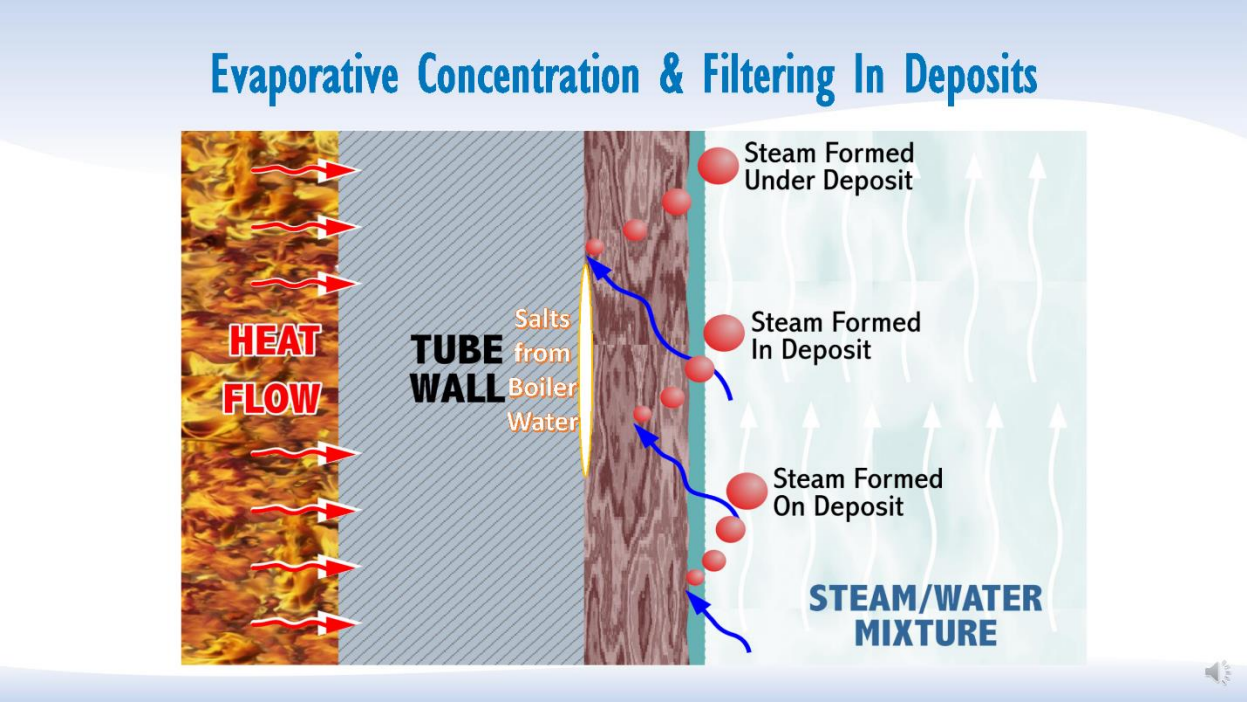


- Underdeposit Corrosion Revealed after Scraping and Vibrating Off All Deposits to Base Metal

This figure shows why underdeposit corrosion occurs. On the right, you have the blue boiler water at the boiling point flowing up the inside of the tube. The furnace heat is at the left, the tube wall is the large gray area, and a thick layer of brown deposits is between the tube wall and the boiler water.

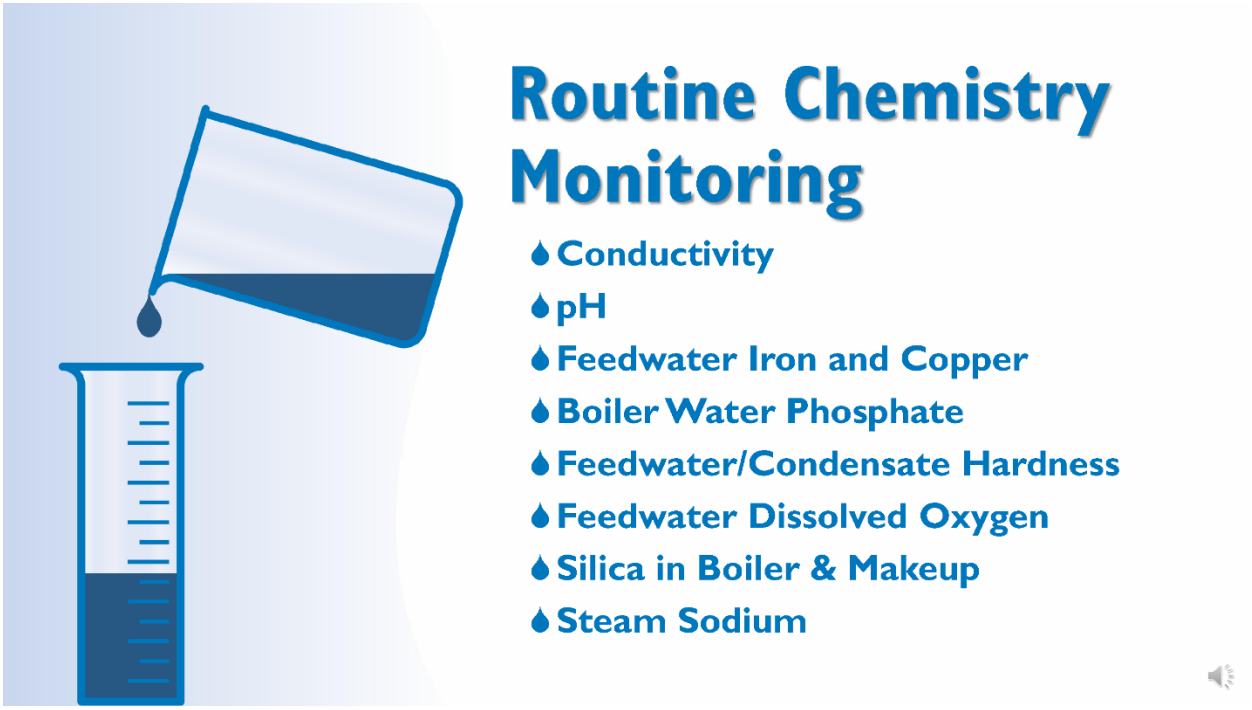
The heat flows through the tube. Heat backs up behind the deposits causing the tube metal temperature to be higher than the boiling point. The water flows through the deposits and the flow is restricted by the deposit layer.

Steam bubbles are generated as the boiler water absorbs heat conducted through the tube metal and deposit layer. As the steam evaporates the dissolve solids from the boiler water remain and are concentrated in and under the waterside deposits. The ultimate case of high heat and excessive deposits would result in dryout in which the boiler water is concentrated to dryness under deposits. Provided deposit weights are limited, water circulation is adequate and heat flux is not excessive. It is typically hypothesized that the boiler water concentration at the tube surface can be 100 to 1000 times more concentrated at the tube surface than in the bulk boiler water.



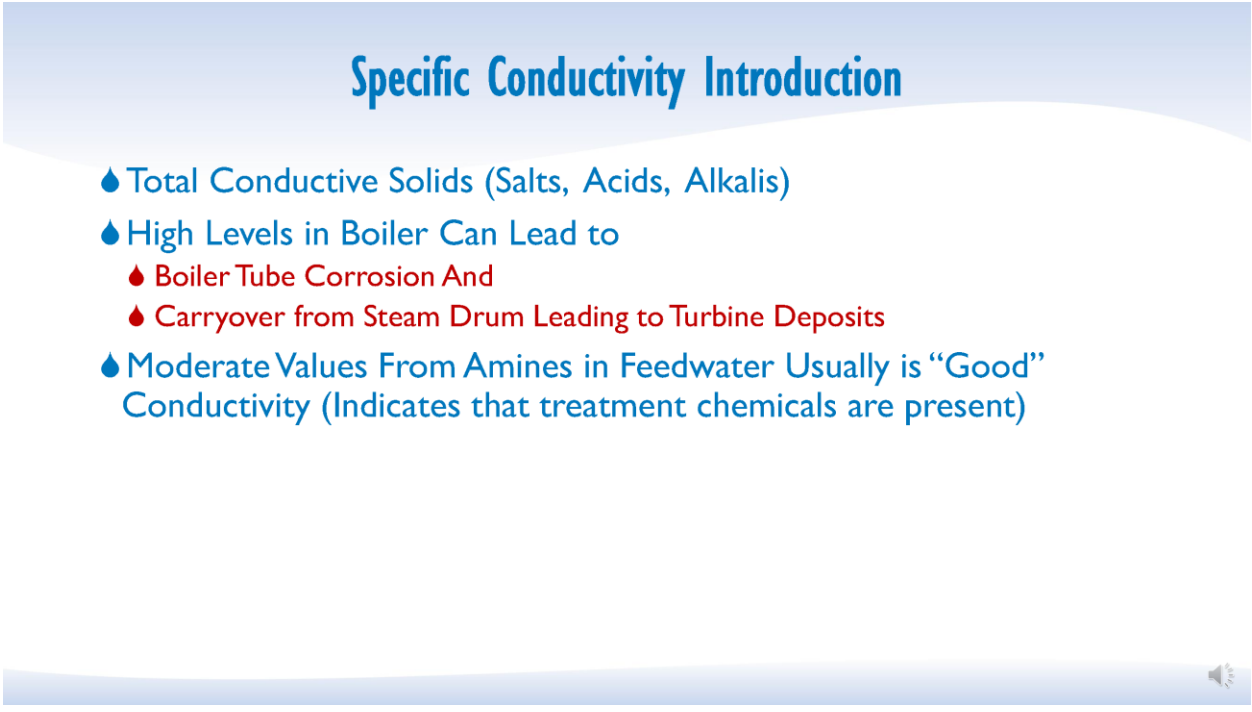
Routine chemistry monitoring in the recovery boiler steam/water cycle normally includes the following parameters:

- Conductivity, which is measured in multiple locations
- pH, which is measured in multiple locations
- Feedwater iron and copper concentrations
- Boiler water phosphate (assuming you are on a phosphate treatment program). All-polymer treatment programs also can be used in recovery boilers.
- Feedwater and condensate hardness concentrations
- Feedwater dissolved oxygen
- Silica in the boiler water and makeup
- Steam sodium

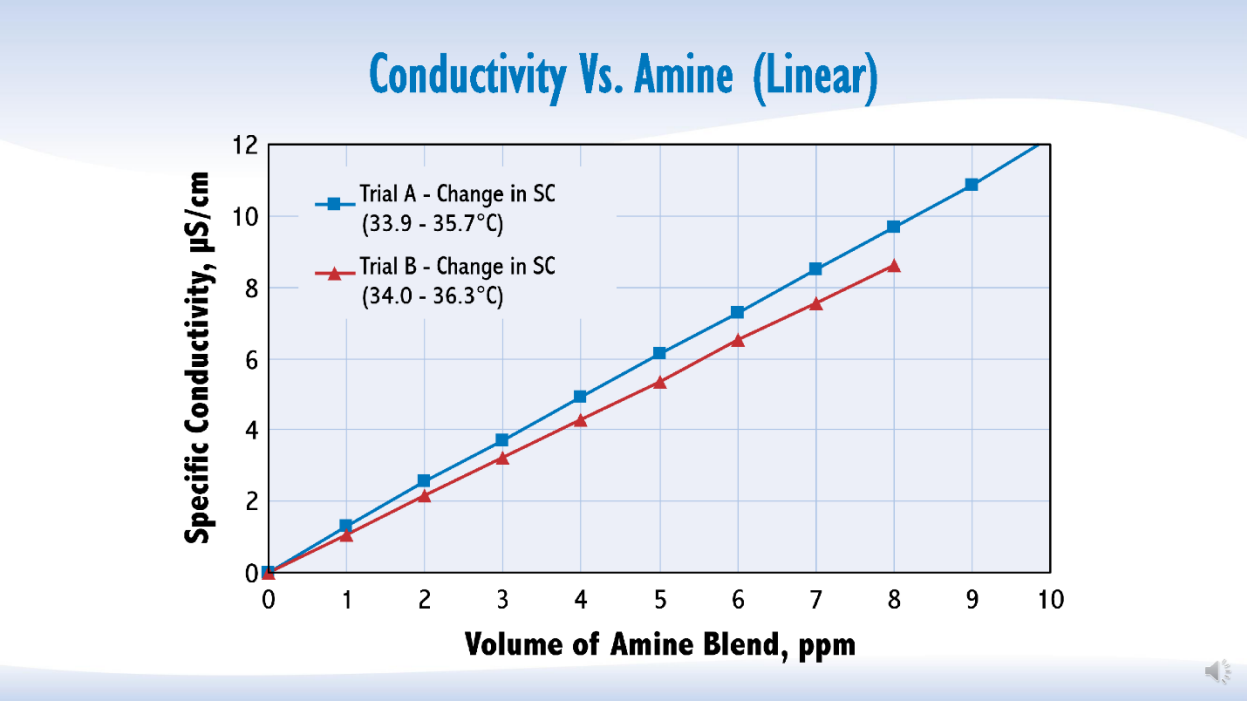


The specific conductivity is a measure of the total conductive solids including salts, acids and alkalis. High levels in the boiler water can lead to boiler tube corrosion and carryover from the steam drum leading to turbine deposits.

Moderate values in the condensate and feedwater is usually considered good because it normally is a reflection that you have the desired amines that are added to raise the pH to limit copper and iron corrosion. You also should have a baseline of conductivity in the boiler water due to treatment chemicals. Thus, bad conductivity is conductivity above the levels expected from treatment chemicals and good conductivity is just due to the treatment chemicals.



This graph 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. The blue line shows in one test that each ppm of amine solution added about 1.2 µS/cm of conductivity. As shown in the graph, the conductivity increases linearly with concentration for most substances. Because the demineralized water used contained some background conductivity, the change (rather than the actual value) in specific conductivity was plotted versus concentration. [While the effect was quite linear for both tests, it is hypothesized that the equalization time and carbon dioxide absorption caused a slightly different rate of change during the test.]



The following lists the typical conductivities in steam/water cycles.

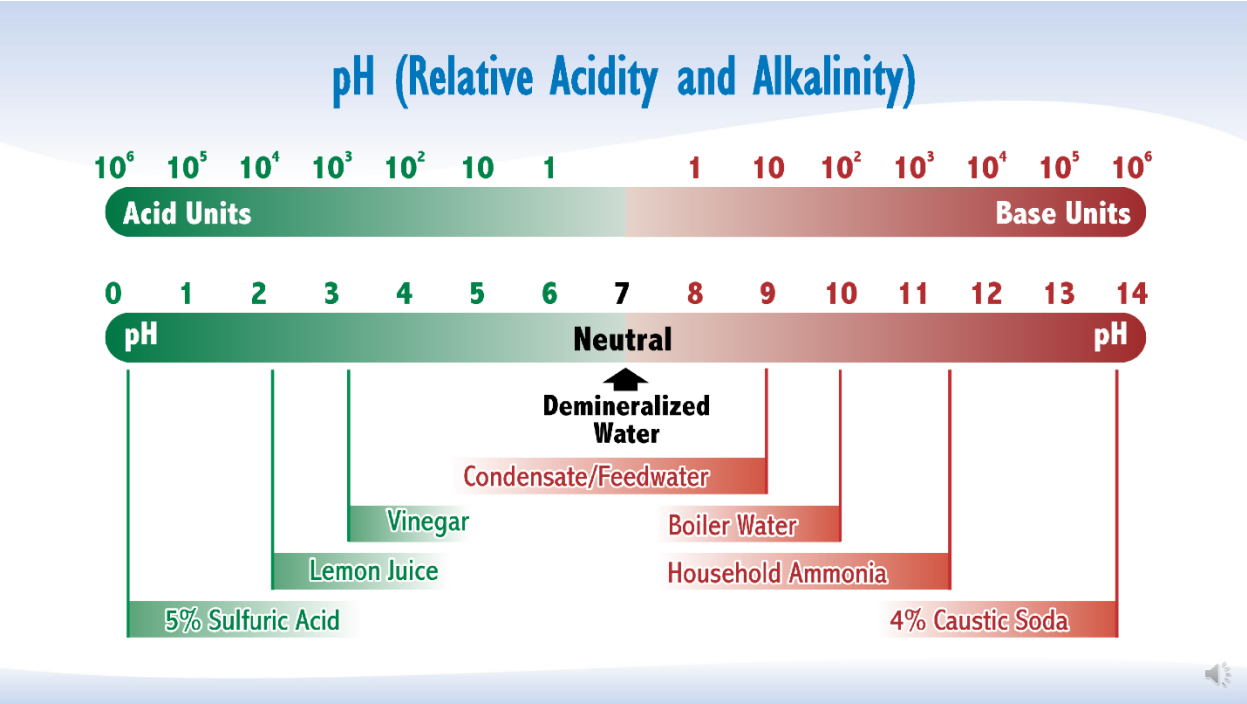
- Pure demineralized water has a conductivity of 0.055 µS/cm at 25°C or 77°F. If the water is colder, the conductivity will be less. If the water is hotter, the conductivity will be greater. Demineralized water in Mills can range from below detection to about 5 µS/cm depending on the type of treatment and performance. Facilities with just a cation and anion exchange in the makeup plant will usually have traces of sodium hydroxide leakage in the effluent. For double pass reverses osmosis systems, the effluent conductivity will normally be mainly due to carbon dioxide.
- Condensate and feedwater conductivities will normally be between 2 and 6 µS/cm and most of that conductivity will be due to the amine blend applied.
- Boiler water conductivities can range from 20 µS/cm to 150 µS/cm. Typically, the boiler water conductivity due to sodium phosphate alone will be 2-5 µS/cm/ppm of phosphate. If you are on dispersant treatment, the sodium salts of the organic dispersant also can impart some additional baseline conductivity.

Specific Conductivity – Typical Values

Sample	Normal Values (a-c) µS/cm at 25°C	Main Source(s)
Demineralized Water	**PURE: 0.055** **RANGE: <0.1-5.0**	RO: Carbon Dioxide (CO_2) IX: Caustic (NaOH) Leakage
Condensate & Feedwater	**2.0 – 6.0**	Neutralizing Amine Feed (e)
Boiler Water	**20 – 150** (d)	2 to 5 x Phosphate, ppm PO_4

(a) Units: µS/cm = µmho/cm
(b) 1 mS/cm = 1000 µS/cm (Caution: Meters Can Auto-Switch Ranges)
(c) The symbol for "micro" is "µ", which can be accessed directly by holding down the Alt key and typing 0181.
(d) Much Higher for Low Pressure Boilers on Softened Makeup
(e) For black liquor contamination in one mill, 5 µS/cm increase corresponded to 5 ppm of black liquor solids and 2 ppm of carbon

The pH is a measure of the relative acidity or alkalinity of a water sample. The conventional scale goes from zero to 14 with 7 being neutral in the middle. Demineralized water that is perfectly pure should be just about 7. Condensate and feedwater pH values will normally have a pH around 9. Boiler water will be closer to a pH of 10. A 4% caustic soda, which is commonly used or regenerating anion resin in makeup plants, has a pH of close to 14. The pH of black liquor also is close to 14. These are 4 orders of magnitude more concentrated than boiler water and can dramatically increase boiler water pH. A 4% sulfuric acid solution, which is commonly used to regenerate cation resin in makeup plants, has a pH of about zero and being 10 pH units away from the boiler water can rapidly and severely lower the boiler water pH. Each pH unit represents a factor of ten in concentration. If the boiler water pH is 10 and acid contamination lower the boiler water pH to 9 in one hour, a continuation of that contamination is expected to result in a pH of less than 4.5 within the next hour. While black liquor itself is caustic and would increase the boiler water pH, evaporator condensate contamination of the boiler water can decompose to organic acids resulting in low boiler water pH values.

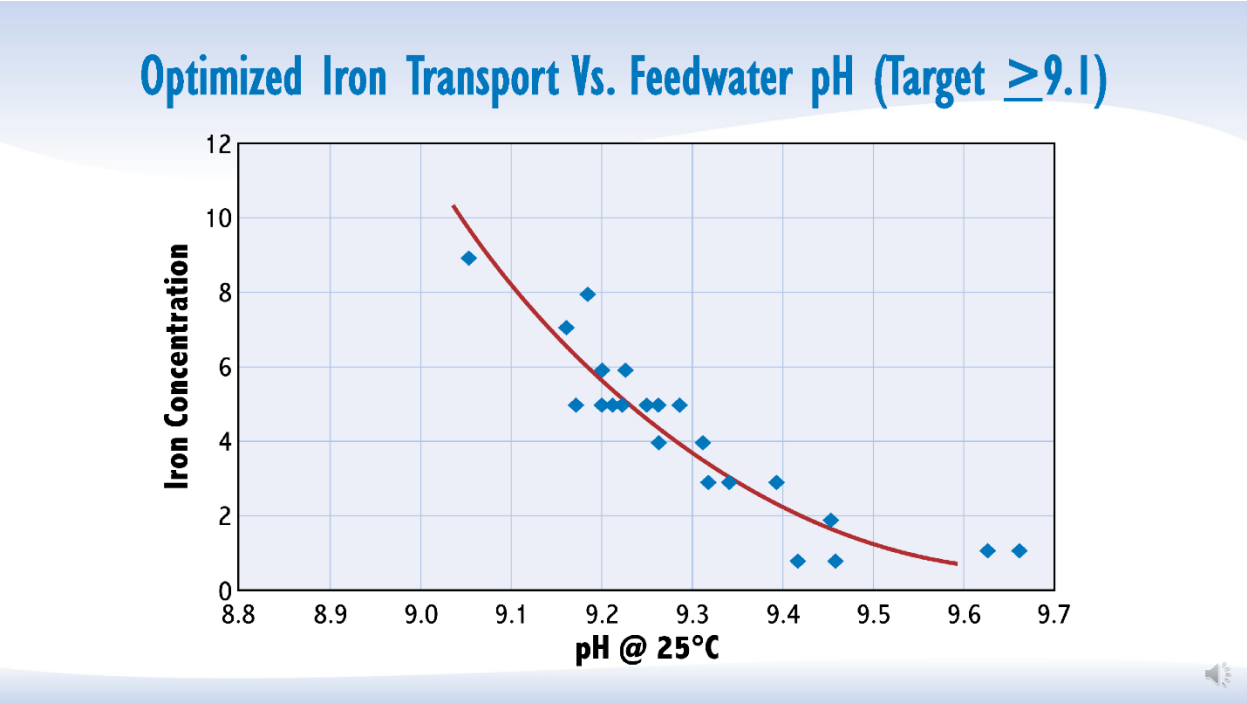


The pH in condensate and feedwater is designed to limit the amount of iron and copper transported to the boiler with the feedwater. This table presents the recommended maximum limits of iron and copper from the ASME Consensus Guidelines. If you have a 1050 psig boiler your iron and copper in the feedwater each should be less than 0.010 ppm or 10 ppb.

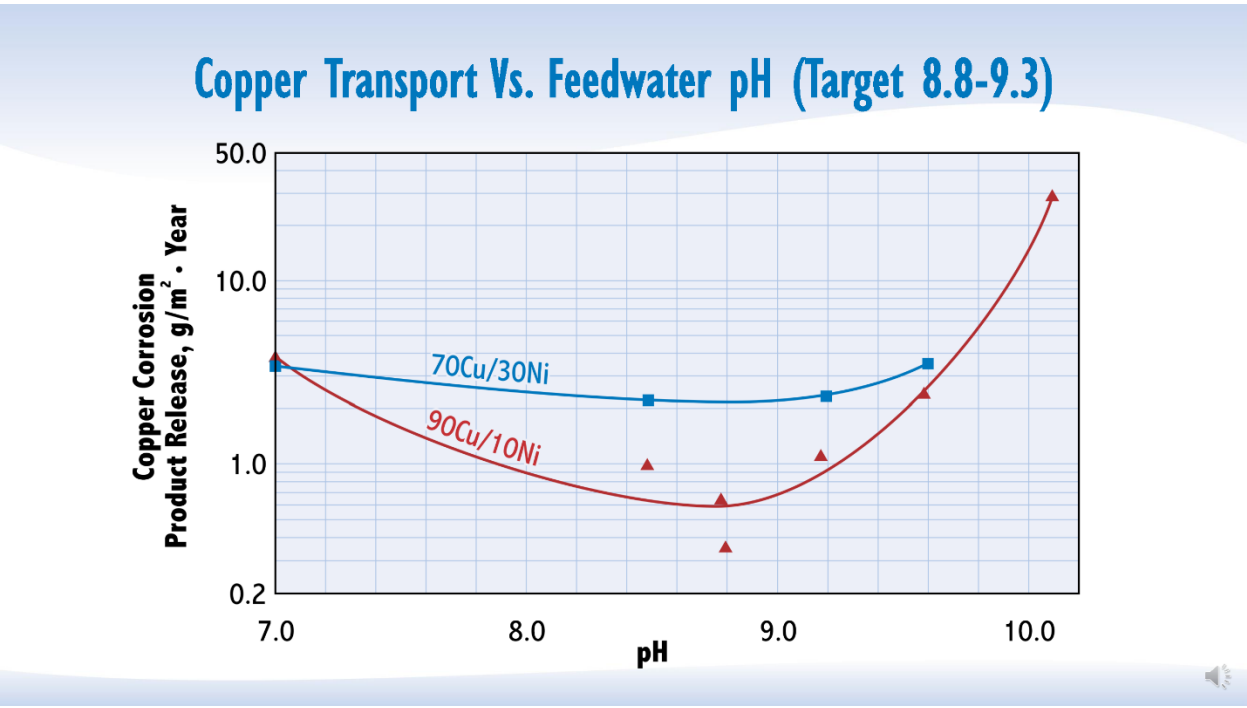
Test Feedwater Iron and Copper Routinely to Verify Corrosion Product Transport is Low, Keep Below ASME Limits

Drum Pressure psig (MPa)	301-450 (2.08-3.10)	451-600 (3.11-4.14)	601-750 (4.15-5.17)	751-900 (5.18-6.21)	901-1000 (6.22-6.89)	1001-1500 (6.90-10.34)
Total Iron, Fe ppm (mg/L)	≤0.05	≤0.03	≤0.025	≤0.02	≤0.02	≤0.01
Total Copper, Cu ppm (mg/L)	≤0.025	≤0.02	≤0.02	≤0.015	≤0.01	≤0.01

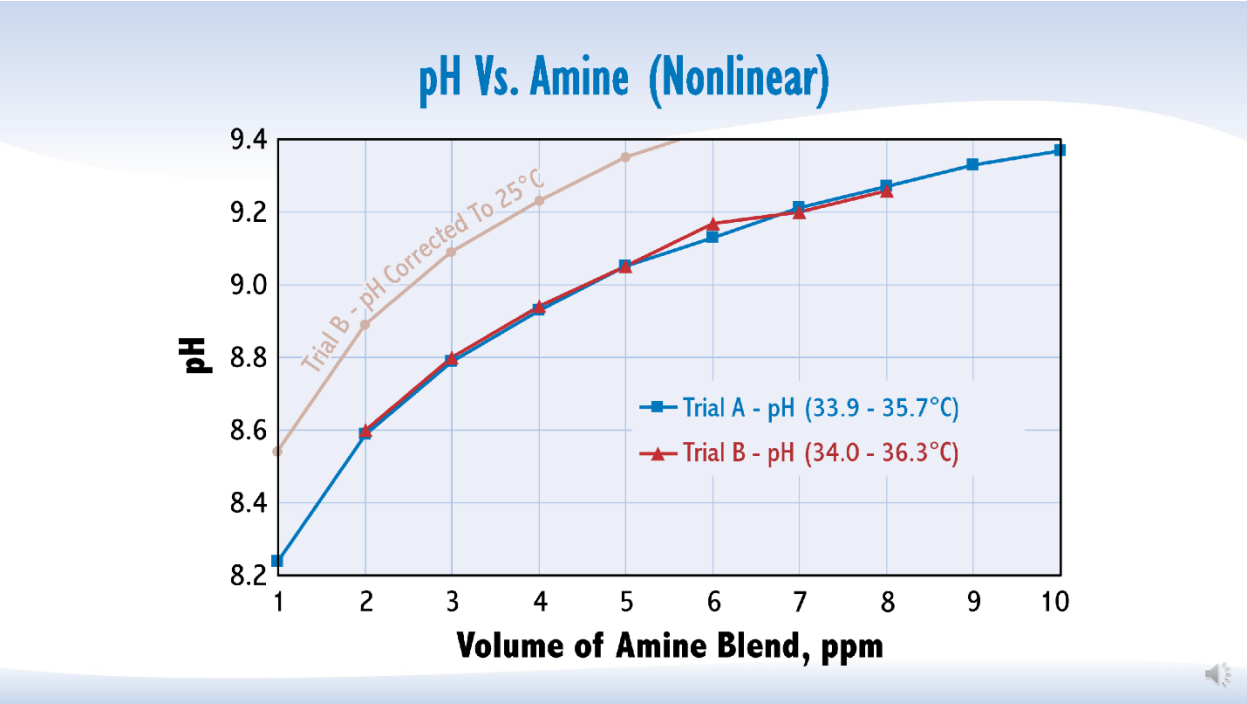
You can achieve about 10 ppb of iron transport at a pH of 9.05 and higher pH values dramatically reduce iron transport.



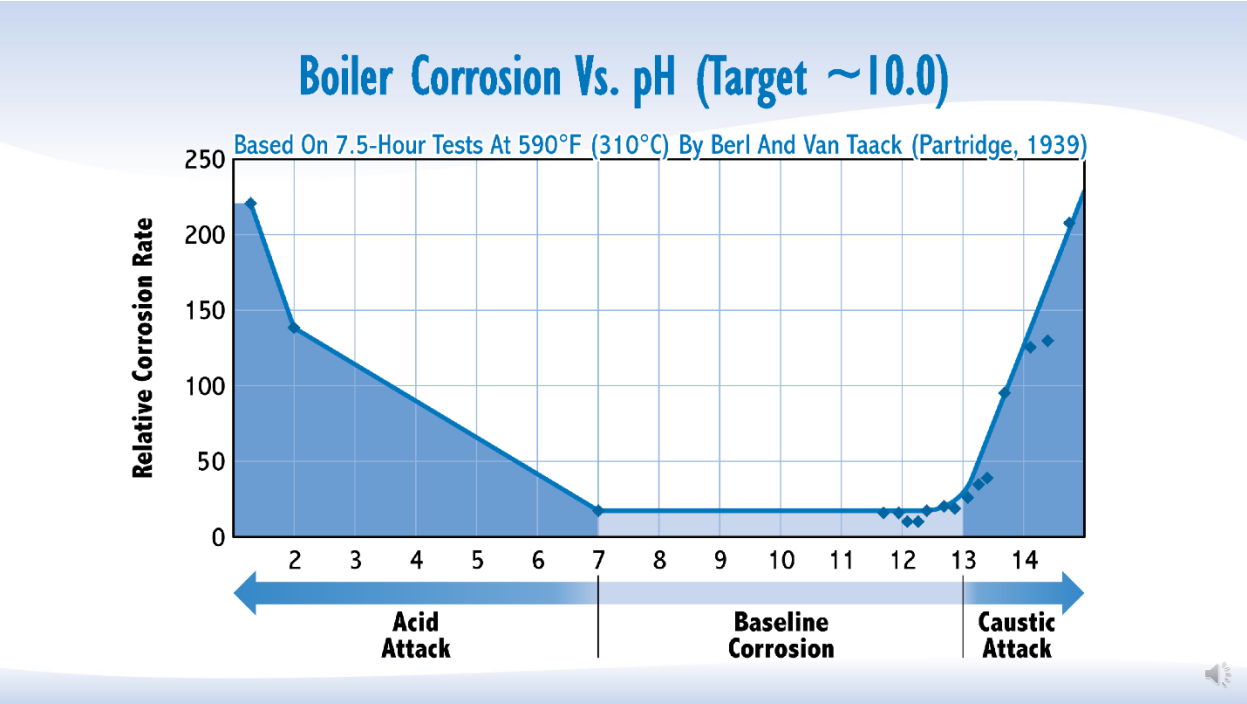
This graph shows a case in which copper transport was minimized at a pH of about 8.8, which has been noted in some operating steam/water cycles. Copper minimization also depends on the types of copper alloys, fluid velocities, dissolved oxygen, oxygen scavenger levels, carbon dioxide and other background contaminant levels. To balance the competing goals of copper and iron transport, the typical target range for feedwater is somewhere around 8.8-9.3. However, some mills have a maximum limit of <9.2 to limit copper transport and some target a pH closer to 9.4 to minimize iron transport.



Condensate and feedwater pH is controlled by feeding an amine. This graph shows the nonlinear changes in pH achieved from different residuals of an amine blend applied to demineralized water. This graph also shows the effect of sample temperature on pH. If you are trying to target a feedwater pH of 9.1 at 25°C that corresponds to about 3.0 ppm of this amine blend. However, in the titration trial the sample temperature was about 35°C and it took about 5.5 ppm of amine to reach a pH of 9.1 at 35°C. To avoid feeding excess chemical and having high copper transport, it is advised to use two stage sample conditioning to achieve a sample temperature of 25°C for pH monitoring. If sample temperature is not 25°C, it is necessary to manually correct for the effect of temperature for any pH readings measured with a bench top meter. The automatic temperature compensation in bench top meters only corrects for the effect of temperature on the electrodes not the effect of temperature on the actual dissociation reactions and pH value.



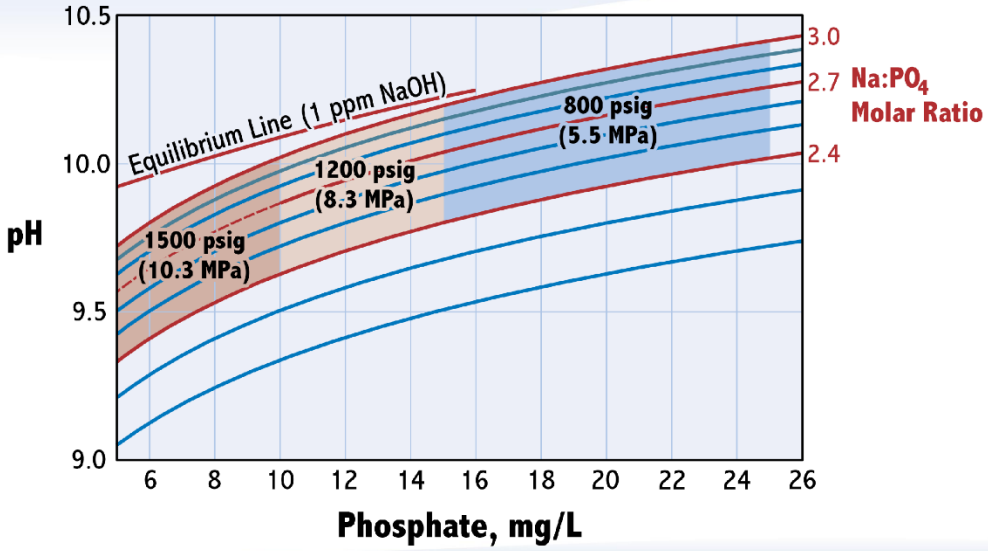
The following curve shows that corrosion rates would be excessive in boilers at low and high pH values. These extremes are not something that could be tolerated even briefly in an operating boiler. The goal is to be in the middle of the baseline corrosion region. Since boiler water is concentrated under deposits by 100-1000 times at the tube surface, the pH at the tube surface can differ from the bulk boiler water by 2 to 3 pH units. If bulk water pH is at a pH of 11, the boiler water pH could be 13 to 14. If the bulk boiler water pH is 5, the pH at the tube surface could be 2-3. To control pH at the tube surface you need tight control of pH, but you also need to keep the boiler clean to avoid even more severe concentration factors. Examples of response procedures to chemistry upsets are shown in TAPPI TIP 0416-05.



This shows examples of a pH versus phosphate concentration control boxes. Each boiler will have curves and a box developed by their chemical contractor, consultant, or subject matter expert. The sides of the control box are bounded by the phosphate concentration target range selected. The top of these particular curves corresponds to trisodium phosphate, which has a sodium to phosphate mole ratio of 3:1. Above this ratio, free caustic is present in the boiler water (a line for 1 ppm of free caustic also is shown) which may increase the potential for caustic gouging in units with heavy deposits. The bottom curve shown for 1200 psig is 2.4. Low ratios (e.g., 2:1 or disodium phosphate) can increase the risk of phosphate gouging or having insufficient buffering against a low pH upset. The key is to stay within your control box. These are just examples, they do not necessarily apply to your boiler.

The power industry has standardized on maintaining ratios at or above 2.85:1 or even 3.0:1 (free caustic range) to avoid phosphate gouging. Such high ratios are usually only required to avoid phosphate gouging in boilers operating above ~1500-2000 psig. However, these higher ratios have been recommended for boilers and heat recovery steam generators operating at lower pressures to minimize the risk of phosphate gouging. The 2.85:1 ratio was recently recommended for a fluidized bed boiler burning bark in a pulp and paper mill based on finding phosphate gouging in some tubes.

Phosphate/pH Control Curve Examples (stay in your "box")



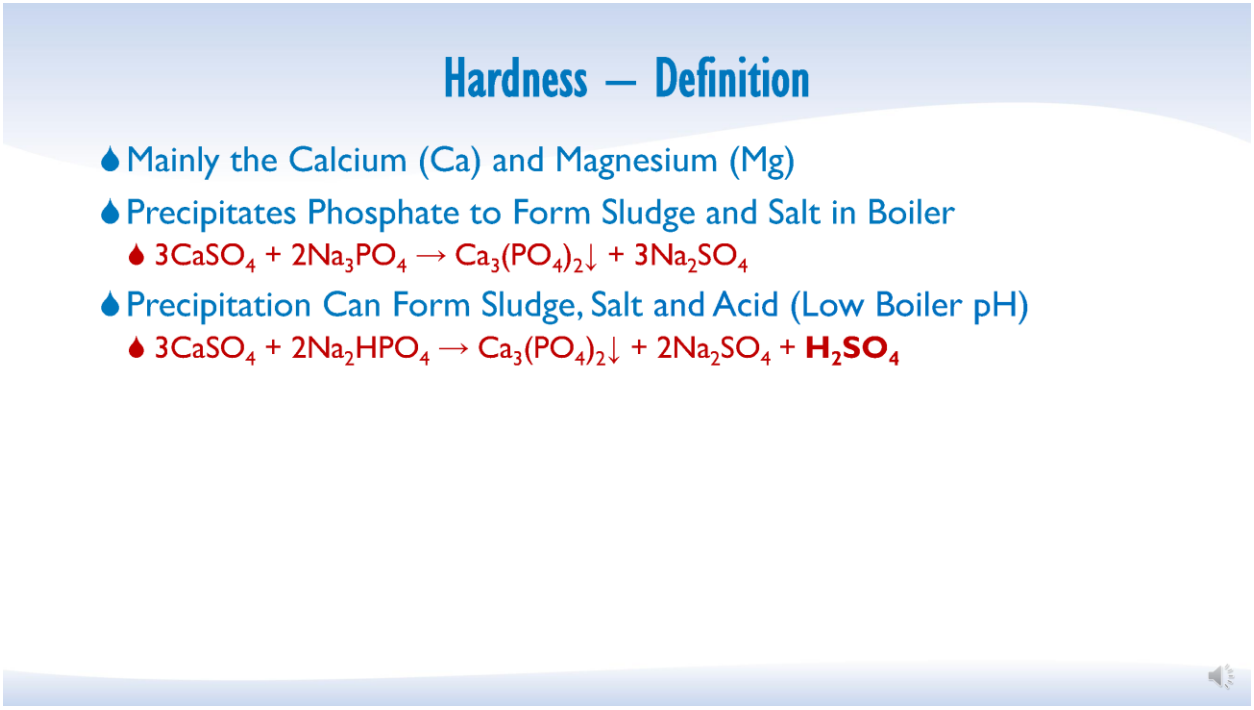
The benefits of phosphate treatment include

- Stabilization of boiler water pH
- Precipitation of hardness as softer, less insulating deposits
- With constant blowdown indicates trace hardness intrusion or a tube leak either of which signals a need for additional diagnostic evaluation.

Benefits of Phosphate (PO_4) Treatment

- Stabilizes pH
- Precipitates Hardness as Softer, Less Insulating Deposits
- With Constant Blowdown, a Decrease in PO_4 Indicates
  - Hardness precipitation (hardness contamination of feedwater)
  - Loss of boiler water (valve/tube leak) – Check!

The two most common forms of hardness entering steam/water cycles are calcium and magnesium. Hardness forms sludge and a salt. For example, calcium sulfate reacts with trisodium phosphate producing calcium phosphate and sodium sulfate. If the boiler pH is low and you have a less alkaline form of sodium phosphate, mill water intrusion may cause acid conditions. This shows calcium sulfate and disodium phosphate resulting in hardness sludge, salt and sulfuric acid in the boiler water. Thus, mill water intrusion can cause a low boiler water pH.



If you have hardness contamination without dispersants, you can see a mass of gray mayonnaise type deposits form in the boiler drums. If you are on dispersant treatment, overall deposition may be less, but you can exceed the capability of a dispersant program, particularly if there is significant silica present. This picture was from a boiler on dispersant treatment with significant hardness and silica contamination. Whether or not dispersants are used, the best approach is to assume all hardness is bad and ensure hardness is below detection to keep the system as clean as possible.

Hardness Deposits

- Without Dispersants, There Can Be A Mass of Gray Mayonnaise Deposits Throughout Boiler Drum
- Hardness Silicate Scale At Right Was In Generation Bank Tube With Dispersant Treatment.
- You can exceed capacity of dispersants.
- All hardness is bad!



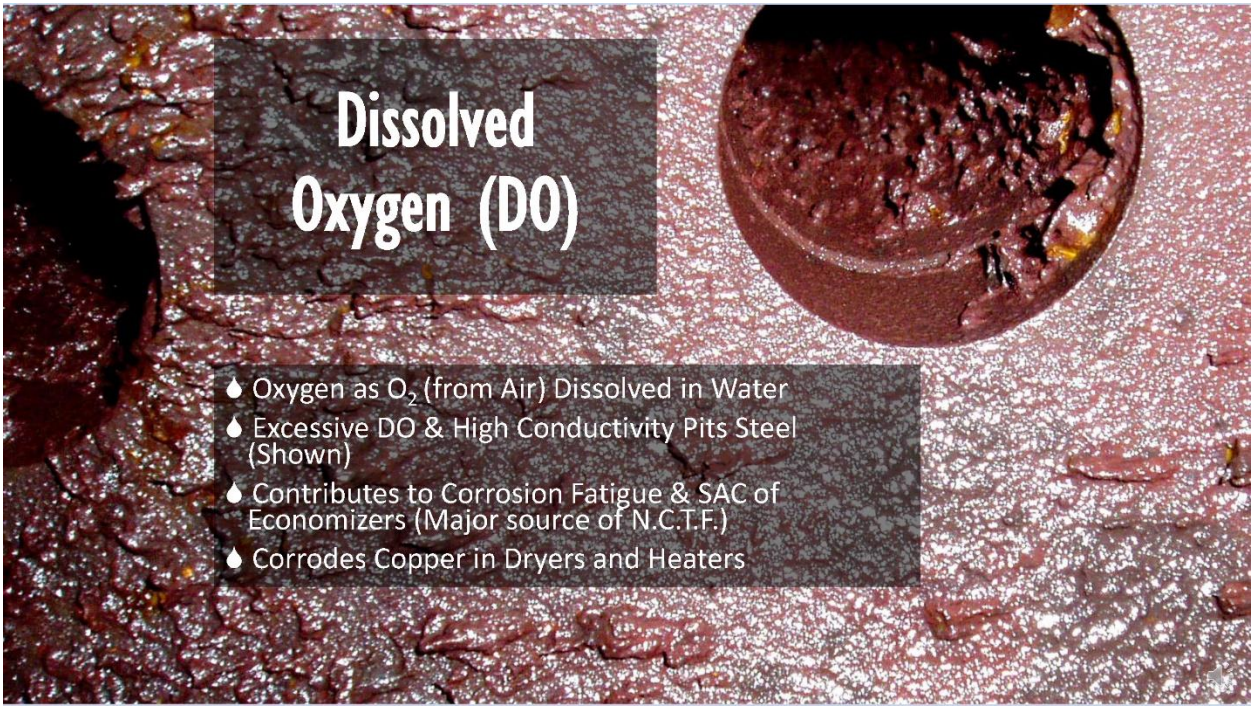
To control hardness, you first need to detect it accurately. Laboratory grade titration systems can detect 0.1-0.25 ppm as $CaCO_3$ of hardness, Do not use the drop tests from the pool supply stores as they have poorer detection limits than titration limits shown here. As shown in the ASME limits, spectrophotometric procedures are required to achieve the detection limits required for boilers operating over 900 psig. Since all hardness is bad, whatever your detection limit, the goal is still to have no detectable hardness, if possible.

Hardness contamination has entered steam cycles from mill water entering through condensate pump seals or boiler feed pump seals, a leaking immersion coil on a domestic hot water tank, hardness contamination of caustic used in anion regenerations, hardness leakage through demineralizers caused by certain polymers in makeup clarifiers, valve leakage in makeup plants, and operating makeup plants beyond exhaustion. Primary methods of control include sewering condensate, regenerating condensate polishers, and eliminate direct injection of mill water to pump seals.

Hardness Control

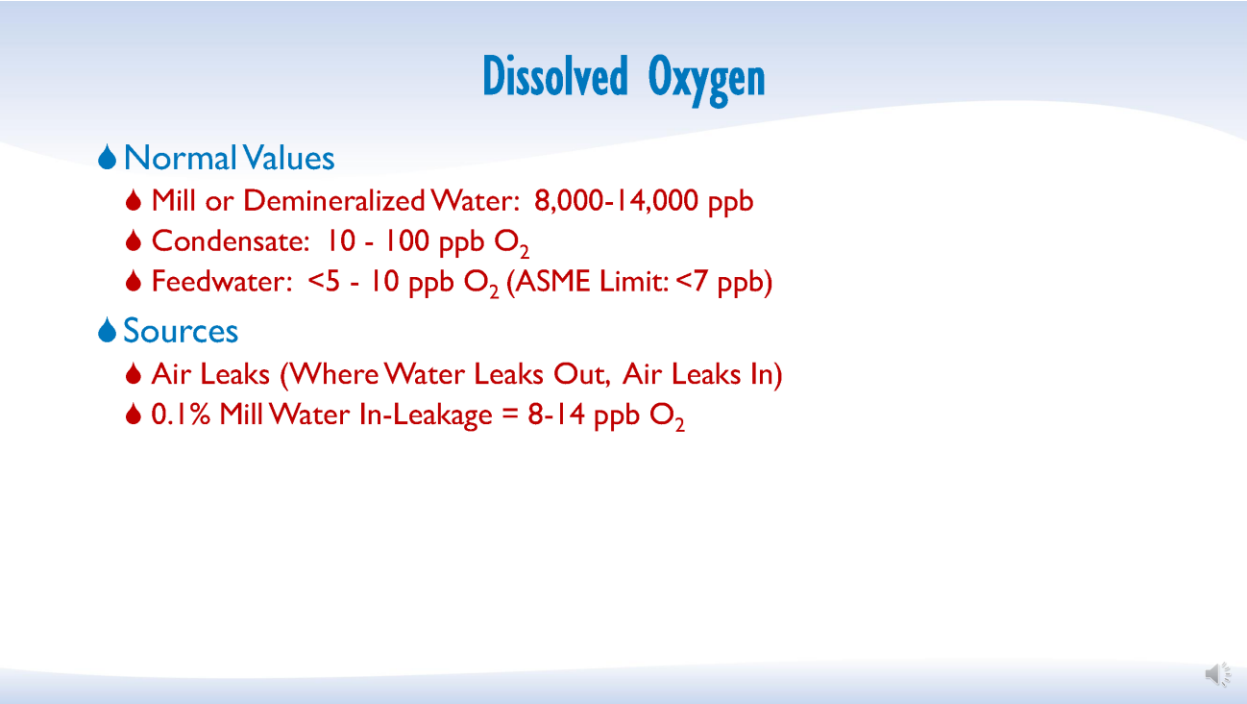
- Detect: ~0.1-0.25 mg/L Titration,<0.02-0.05 mg/L Spectrophotometry
- ASME Limits: <0.2 451-750 psi, < 0.1 mg/L 751-900 psi, <0.05 mg/L 901-1000 psi, >1000 psi (NONE)
- Expected Values (ppm $CaCO_3$) = **NONE**
- Sources
  - Mill Water Contamination (of Condensate/Feedwater)
  - Problem In Makeup Demineralization System
- Controls
  - Dump Valves to Sewer Condensate
  - Condensate Polishers (IX Softeners) To Remove Hardness

Oxygen is present in air at about 21% by volume which corresponds to 230,000,000 ppb on a weight basis. Oxygen dissolves in water and excessive concentrations combined with salt can lead to dissolved oxygen pitting like that shown here for a lower pressure recovery boiler with softened makeup. For higher pressure recovery boilers, the combination of dissolved oxygen, stress and sometimes low pH can combine to contribute to corrosion fatigue (CF) or stress assisted corrosion (SAC) in economizers, which have been common causes of noncritical tube failures in economizers. Dissolved oxygen in steam and condensate also contributes to copper corrosion in heaters and coolers in the mill.

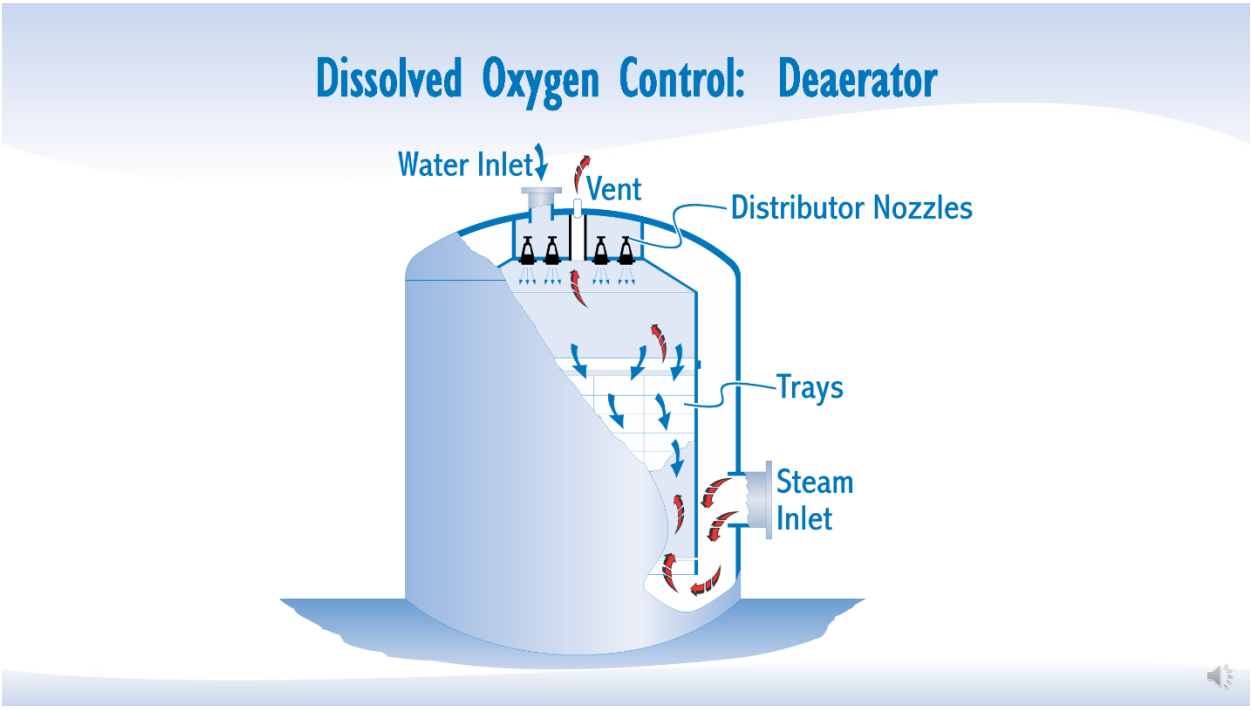


The solubility of dissolved oxygen ranges from about 8000 ppb for warm climates to 14,000 ppb near the freezing point. This is about how much you will have in your mill water. Feedwater should have <5-7 ppb of dissolved oxygen and condensate will often pick up a little bit from air leaks in the system and have about 10-100 ppb of dissolved oxygen.

The main source is air. Where water or steam leaks out, air diffuses in the opposite direction. The other source can be from mill water intrusion. Just 0.1% mill water intrusion can introduce 8-14 ppb of dissolved oxygen.



The primary method of control of dissolved oxygen is through mechanical deaeration in a deaerator. Water enters the top through a water inlet chest. It pushes the spray nozzles down to form cones of water droplets, which gives you lots of surface area in the spray section. Steam entering the side of the vessel is directed to the bottom of the tray box. The steam flows up through a series of alternating trays and then heats the water spray up to the boiling point. The small excess of steam leaving the deaerator carries the noncondensible gases out the deaerator vent. The water droplets heat up while dropping through the steam and I have been told that it reaches the boiling point by about the top 2 or 3 tray rows. Then, this boiling water cascades down through the trays with a counter current flow of steam. The tray section is a counter current steam stripper to complete the removal of dissolved oxygen.

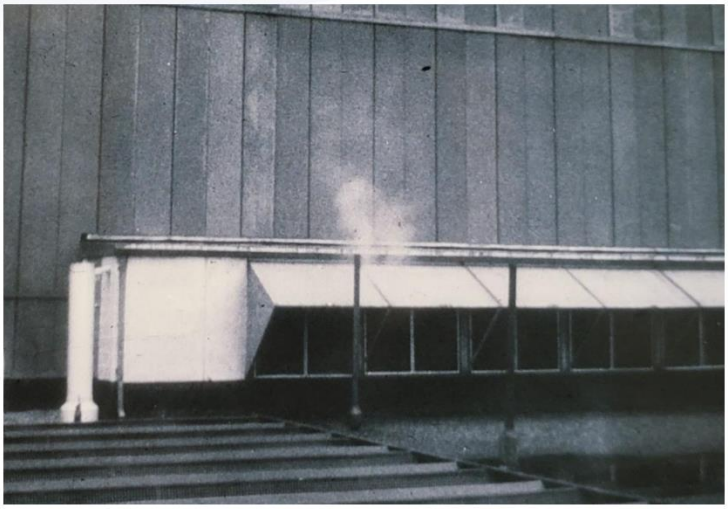


This is an example of a vent as found before changing the vent orifices and the deaerator effluent dissolved oxygen was elevated despite the high venting rate.



After they went through a number of trials, they found that the deaerator worked best with fairly minimal deaerator venting as shown by the low vent flow in this figure which had achieved 2 ppb of dissolved oxygen without the feed of an oxygen scavenger. I have seen deaerators working well with much greater amounts of venting, so the lesson learned is to experiment with different venting rates until you find the one that provides the best performance.

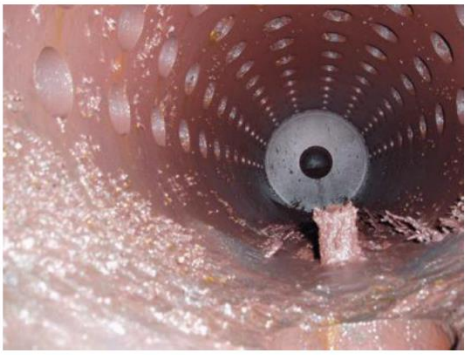
2 ppb Dissolved Oxygen with No Scavenger (0.3125 Inch Orifice)



Deaerators are designed to achieve their rated performance at a fixed set of design conditions. When operating at other flows higher than design dissolved oxygen levels can be experienced. To ensure low dissolved oxygen levels, an oxygen scavenger is applied to the deaerator effluent to reduce residual dissolved oxygen. The oxygen scavengers also can react with metal oxides to Inhibit pitting of steel (this is from a low-pressure recovery boiler on softened makeup) and promote the formation of a protective, dull gray oxide layer (same economizer inlet header after problems with deaerator were corrected).

Oxygen Scavengers – Reducing Agents

- Oxygen Scavenging: Reduces Residual Oxygen After Deaeration
- Metal Oxide Reduction: Orange or Red Rust → Gray Rust





For units with elevated dissolved oxygen levels or insufficient oxygen scavenger residuals pitting, SAC or CF of the economizer may occur. High dissolved oxygen can also contribute to copper corrosion in the steam/condensate system.

An excessive feed or residual of scavenger can lead to flow accelerated corrosion (FAC) of carbon steel. FAC is a reducing dissolution type mechanism occurring in high velocity areas particularly those operating at temperatures of 300°F. This shows FAC of a deaerator floor. Affected metal surfaces are essentially free of any protective oxide (appear to be almost polished) and can have pock marks as shown here. If you see this, then you should consider evaluating the system for other areas that may be susceptible to damage as FAC has caused fatal failures of piping in high pressure condensate and feedwater systems in the power industry. The other concern with an excessive feed of oxygen scavenger is that it creates decomposition products that can increase background conductivity and contribute to corrosion.

Oxygen Scavenger Feed and Residual

- Underfeed (or insufficient residual)
  - Pitting, SAC, or CF of Economizer
  - Copper Corrosion in Steam/Condensate System
- Excessive feed or residual
  - **FAC**: Flow Accelerated Corrosion (e.g., of Deaerator Floor)
  - Thinning & Failure of Feedwater Piping
  - Decomposition Products (Conductivity)



While corrosion product formation and transport from the condensate and feedwater system is primarily determined by controlling levels of pH, dissolved oxygen, reducing agent, and turbulence, film forming products also can and have been applied to reduce corrosion product transport. The original filming amines, such as octadecylamine, had a tendency to strip off surfaces during pH swings causing mud balls of or waxy corrosion products to accumulate in condensate polishers, steam traps, and boiler drums. However, film forming products are experiencing a resurgence in the power industry and other steam cycles. These rely on newer filming amines and other non-amine film forming products which are less likely to suffer from the mud ball problem of their predecessors. Information is available in the cited reference (16).

The boiler water silica should be monitored and controlled to limit steam silica to <20 ppb as SiO_2. This table presents the silica limit calculated for the indicated drum pressures and pH values. For example, if operating at 900 psig the boiler water silica should be less than 7.8 ppm to ensure less than 20 ppb of silica in the steam. At 1500 psig, the silica should be less than 1.7 ppm. There are curves in the TAPPI Tip 0416-03 that enable you to determine the amount of silica carryover due to volatilization at other pH values and boiler pressures. This table considers both the volatile carryover of silica and the mechanical carryover of silica. Appendix A in Reference 8 provides a method to consider volatility and mechanical carryover. The power industry tends to set lower boiler water silica levels than indicated by the sources referred herein.

Monitor/Control Boiler Water Silica to Keep Steam Silica < 20 ppb
(& online silica monitor in makeup to control SiO_2 entering cycle)

Drum Pressure psig	Boiler Water Silica ppm SiO_2	Boiler pH Assumed in Calculation
750	9.0*	10.0
900	7.8	9.8
1000	5.9	9.7
1250	3.1	9.7
1500	1.7	9.5

*Calculated Value Was 12.9 ppm for pH of 10.0, but 2.5 ppm $CaCO_3$ of Caustic Alkalinity per ppm SiO_2 is Suggested if Boiler Water Silica Normally Exceeds ~9 ppm. The 9.0 ppm limit assumes no free caustic.

Having completed the recovery boiler water treatment course, you should

- know the goals of recovery boiler water treatment and the effects of deposits,
- be familiar with the basic components of the steam/water cycle, and
- know the common routine chemistry monitoring to protect recovery boilers including conductivity monitoring at all points to limit total dissolved solids in the cycle (with dump valves on key contamination sources), pH monitoring at all points to control corrosion, boiler water phosphate to buffer the boiler water pH, feedwater and condensate hardness to avoid precipitating out the phosphate buffer, feedwater dissolved oxygen to protect the economizers, and feedwater iron and copper, which are the main sources of deposits in the boiler.
- understand that it is important to maintain steam sodium and silica at low levels to avoid turbine deposits, with the sodium measured directly and the steam silica usually inferred by monitoring and controlling boiler water silica.

One last item that is mentioned in closing is that there have been some recovery boilers which have had significant carbon-based deposits that can be very insulating and very difficult to remove. To reduce the risk of those deposits, it is suggested to keep boiler water color less than <20 CoPt units.

Recovery Boiler Water Treatment Course Goals

- Know Treatment Goals and Understand Effects of Deposits
- Be Familiar with Basic Components of Steam/Water Cycle
- Know Common Routine Monitoring to **Protect Recovery Boilers**
  - Conductivity µS/cm (all points with auto-dump valves on bad streams)
  - pH (all points)
  - Boiler Water Phosphate, ppm PO_4
  - Feedwater/Condensate Hardness, ppm $CaCO_3$
  - Feedwater Dissolved Oxygen, ppb O_2 (and Oxygen Scavengers)
  - Feedwater Iron (Fe) & Copper (Cu) (Main source of deposits in boilers)
- Maintain Pure Steam: <10-20 ppb Na (Sodium) & <20 ppb SiO_2 (Silica)

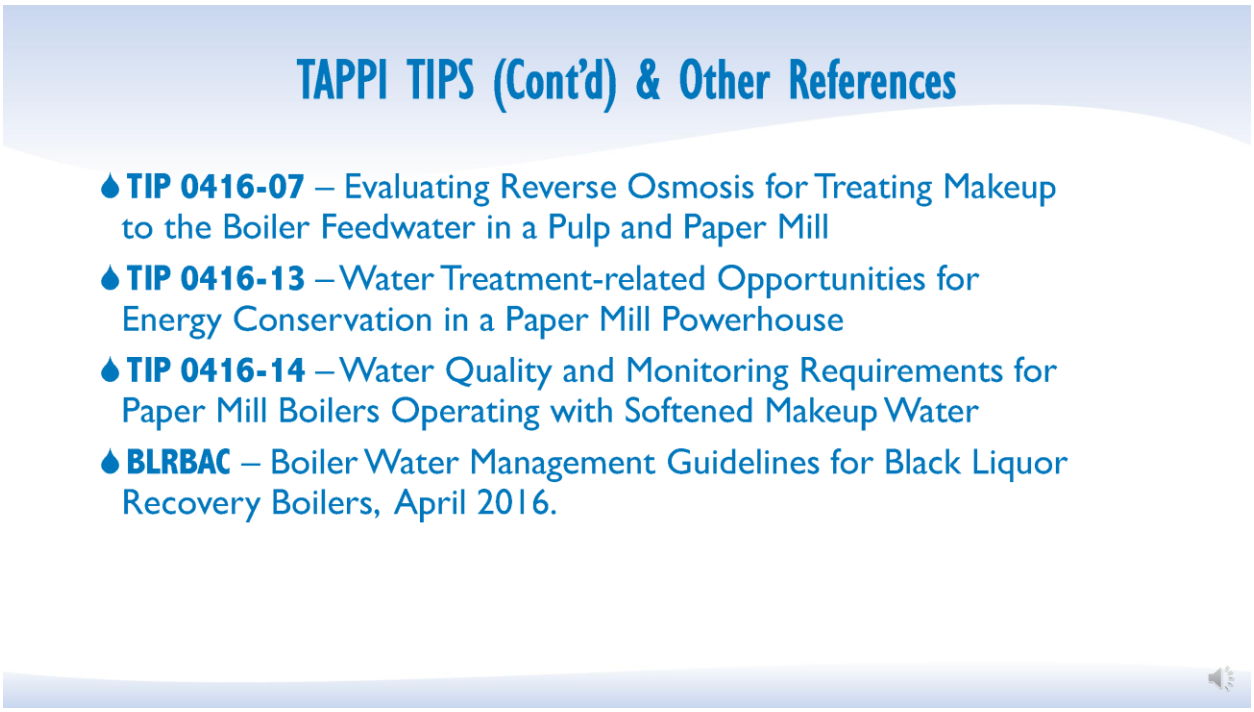
NOTE: While not commonly practiced, I advise keeping Boiler Water Color <20 CoPt. This may help you avoid nasty, carbon-based deposits

If you would like more information, there are Technical Information Papers from TAPPI called TAPPI TIPS. A few worth highlighting are TIP 0416-03 which presents the silica curves that were mentioned in the presentation as well as a different type of phosphate treatment control curve called congruent treatment and TIP 0416-05 which presents responses to chemistry upsets.

Want More? 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 0416-14, also may be of interest because it provides limits for recovery boilers receiving softened makeup, which was not the focus of this course. BLRBAC also has a document that presents a lot of guidance related to recovery boilers.



SUPPLEMENTAL INFORMATION 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 the presentation. 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).
- **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.
- **Na**: Sodium is a standard online analyzer on the inlet to condensing steam turbines. Industrial steam turbine suppliers typically have steam sodium limits of 5 to 20 ppb. Problems with steam sodium deposition are common if steam sodium is over 20 ppb (1) and units with significant free caustic in the boiler water have reported problems with steam system deposits above 10 ppb. In addition to reduced turbine efficiency and capacity, sodium deposits can lead to stress corrosion cracking of steam turbines and stainless steel expansion bellows.
- **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 (typically reported in NTU, nephelometric turbidity unit, FTU, Formazin Turbidity Unit, or FNU, Formazin Nephelometric Unit). An indication of colloidal and suspended matter. It directly measures the light scattered at a 90 degree angle. Older 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 Fe = 5-100 NTU)(2). This corresponded to 20 ppb Fe of iron oxide per NTU of turbidity - although it may become less linear at lower (<100 ppb) concentrations. The newer online meters use lasers or near infrared wavelengths (17). In 2023, Vepsäläinen and Skovbjerg reported on studies in steam/water cycles at nuclear and fossil power plants using online turbidimeters and laser turbidimeters indicating correlations of 32.1 ppb Fe/FNU and 58.5 ppb Fe/FNU for two plants and stated that the correlation is plant specific (17). Also, one graph for a single plant indicated that 1 FNU corresponded to iron readings from ~20 to ~60 ppb Fe and the correlation fit for that facility showed that 0.5 FNU corresponded with 20 ppb Fe (17). Benchtop spectrophotometers cannot measure true turbidity, but they often can provide turbidity indications and results are presented in FTU. 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. For modern instruments and calibration methods, more stringent limits would be appropriate.
- 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 below detection.

- 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.

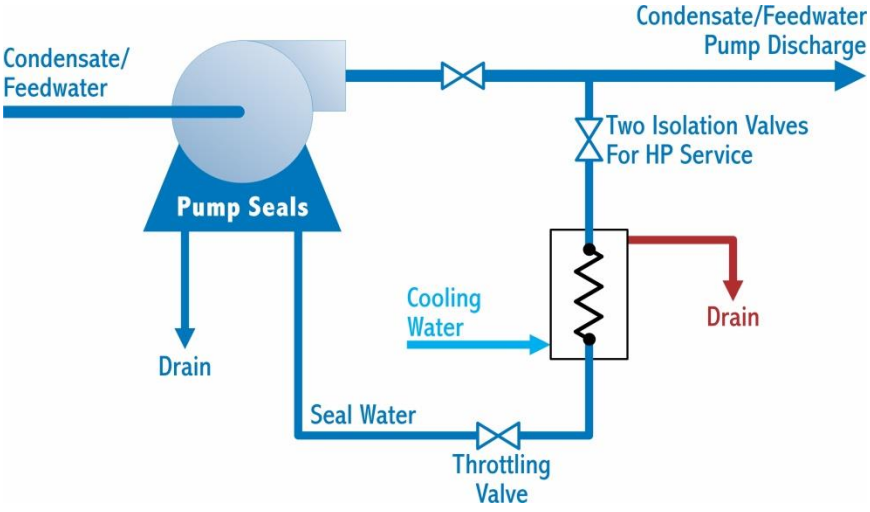
The preceding analyzers have been used for decades, although some were used to a lesser extent in the pulp and paper industry. TIP 0416-03 (and its predecessor documents back to 1984) recommends minimum grab-sample sample frequency of only once per shift, but it suggests these on-line analyzers in the 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.

Hardness Control Option

The following figure (not included in oral presentation) provides an example of a seal water retrofit which has been implemented at numerous facilities to eliminate a source of hardness contamination.



Other Learning Opportunities

Recovery boiler water treatment requires an understanding of much more than the steam/water cycle chemistry. One needs to have an understanding on all facets of the steam/water cycle. As indicated in the following list, to properly provide training on these topics would require more detail on the areas covered as well as additional training modules.

- Makeup Water Treatment
- Condensate Collection and Treatment
- Chemical Cleaning

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