

# RECOVERY BOILER WATER TREATMENT

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## 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.

## INTRODUCTION

### Presentation Format

Figure 1 presents an outline for today's discussion. This presentation first tries to present an introduction to some of the basic chemical parameters and principles that a water treatment operator in the recovery area should understand. They are designed to be consistent with the current TAPPI guidelines related to boiler water and steam/water cycle chemical treatment programs (1-4).

#### Figure 1 - Presentation Format

- ◆ Objectives of Treatment Program
- ◆ Steam/Water Cycle: Basic Components
- ◆ Top Routine Chemistry Parameters
- ◆ Summary

Due to the time limitations of this presentation, a series of appendices are provided with more in-depth discussions for supplemental study or future reference. These appendices include information on makeup water treatment, condensate and feedwater treatment, boiler water treatment, steam purity, preventive maintenance, personnel training, and chemical cleaning of boilers.

### 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	Deposits	Corrosion
Condensate System	--	Minor
Feedwater System	--	Minor
Boiler	Minor	0 or Minor
Superheaters	0	0
Turbines	0	0

Waterside deposits in boiler tubes raise tube metal temperatures and can lead to tube failures from overheating and waterside and fireside corrosion. Waterside corrosion also 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 3-5 present examples of waterwall tube deposits, overheating, and corrosion in an oil fired boiler, bark fired boiler, and a black liquor recovery boiler, respectively (from three separate mills).

**Figure 3 - Boiler Deposit Example**



- ◆ Thick Nose Tube Deposits of Copper and Copper Oxides Over Mixed Iron Oxide, Hardness Phosphate and Carbon

During operation, the tube in Figure 3 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 3 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.

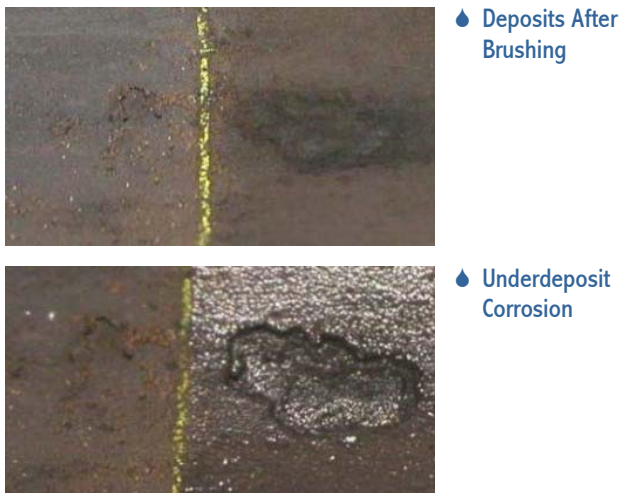
Figure 4 presents an internal view of a bark fired boiler tube that had severe waterside deposits about 1-2 feet over the firing grate, and the tube failed due to short-term overheating (blistering) on the hot side surface. The boiler experienced a rash of failures and had to be chemically cleaned on 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 4 - Boiler Blistering Example**



Figure 5 shows a localized deposit in a recovery boiler tube which resulted in underdeposit corrosion.

**Figure 5 - Boiler Corrosion Example**



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. 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.

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. See Appendix D for more detailed discussions of the effect of deposits on tube temperatures, short-term (blisters) and long-term (creep) overheating, waterside and fireside corrosion, and chemical cleaning of boilers.

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.

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 6 presents an example of turbine deposits. The deposits shown in Figure 6 did not actually result in any detectable damage to turbine components.

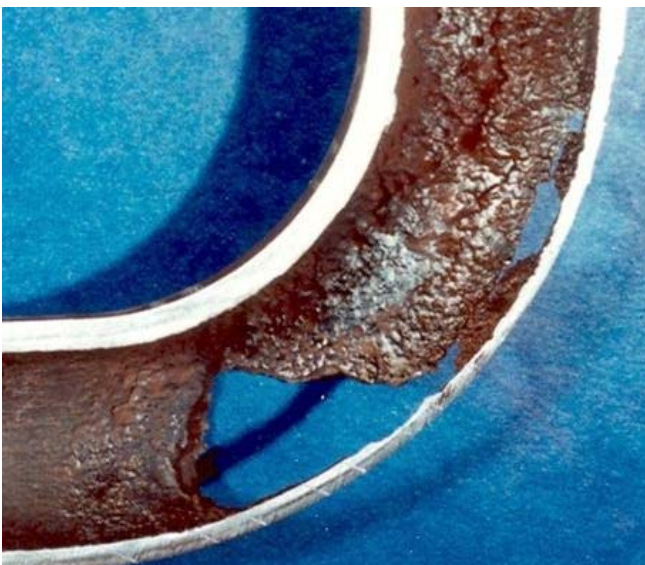
The damage in Figure 7 shows a primary superheater which failed after about 6 months of corrosion occurring during operation. This was the first bend in the gas pass in a boiler that was experiencing carryover. This was the second superheater lost on this boiler in 6 months after a boiler water chemistry 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 6 - Turbine Deposits Example**



**Figure 7 - Superheater Corrosion 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 8 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. It also includes recommended sampling and on-line monitoring. These are discussed in subsequent sections of the presentation or appendices.

## 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 8. The key for this figure is presented below.

- 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 ( $\mu\text{S}/\text{cm}$ ) or micromhos per centimeter ( $\mu\text{mhos}/\text{cm}$ ). 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  $\mu\text{S}/\text{cm}$  to  $\text{mS}/\text{cm}$ , where 1  $\text{mS}/\text{cm}$  is 1000  $\mu\text{S}/\text{cm}$ . Read the fine print on the digital readout - as this can delay proper response during major chemistry upsets. Boiler water can be 20-150  $\mu\text{S}/\text{cm}$ , condensate, feedwater and steam can be 2-10  $\mu\text{S}/\text{cm}$ , and demineralized makeup can be 0.05 to 5.0  $\mu\text{S}/\text{cm}$ , depending on system requirements and capabilities. Plants with softened makeup have much higher values.
- CC: Cation Conductivity (also in  $\mu\text{S}/\text{cm}$ ) 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. Values should be low (e.g., <0.2-0.5  $\mu\text{S}/\text{cm}$ ) 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).



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 is 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 9 presents some of the top chemistry tests. Additional tests required for chemistry control are discussed in Appendix F.

### Figure 9 - Top Routine Chemistry Tests

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

(Color, Turbidity, Silica, Iron/Copper Corrosion Products, Sodium, Alkalinity - See Notebook)

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 such as the Specific Conductivity, summarized in Figures 10 and 11:

### Figure 10 - Specific Conductivity

- ◆ Total Conductive Solids (Salts, Acids, Alkalis)
- ◆ High Levels Can Cause Foaming and/or Corrosion
- ◆ Units: Usually  $\mu\text{S}/\text{cm}$
- ◆ Micromho ( $\mu\text{mho}/\text{cm}$ ) = Microsiemen ( $\mu\text{S}/\text{cm}$ )

- ◆ Millimho ( $\text{mmho}/\text{cm}$ ) = Millisiemen ( $\text{mS}/\text{cm}$ )
- ◆  $1 \text{ mS}/\text{cm} = 1000 \mu\text{S}/\text{cm}$  (Beware of auto-switching ranges on meter!)

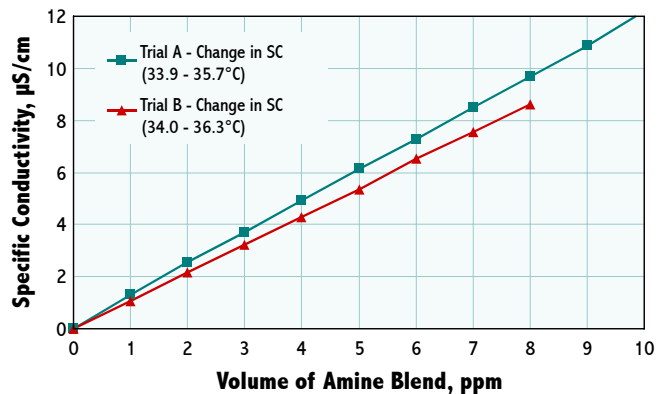
### Figure 11 - Specific Conductivity

Sample	Normal Values $\mu\text{S}/\text{cm}$	Main Source
Demineralized Water	0.05 - 5.0	NaOH Leakage
Condensate & Feedwater	2.0 - 6.0	Amine Feed
Boiler Water	20 - 150 (a)	3 to 5 $\times$ $\text{PO}_4$

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

Figure 12 presents an example of the effect of an 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 12 - Example of Amine Blend Effect on Conductivity



## pH

Figure 13 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 (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 13 - pH (Relative Acidity and Alkalinity)**

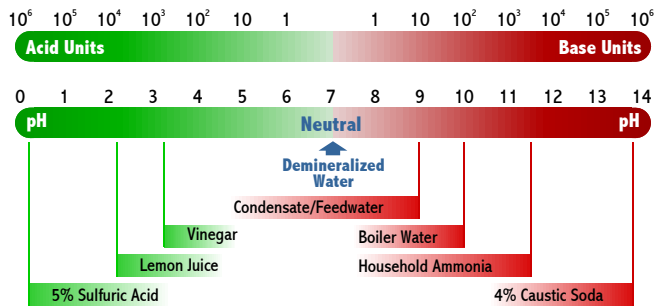


Figure 14 shows the effect of the amine blend tested in Figure 12 on the pH values of a sample of slightly alkaline demineralized water. The greatest change in pH values was noted up to about a pH of about 9.0-9.1 or about 4.5-5.5 ppm of the amine blend. Thereafter, the rate of pH increase decreases 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 14 (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 14 - Example of Amine Blend Effect on pH**

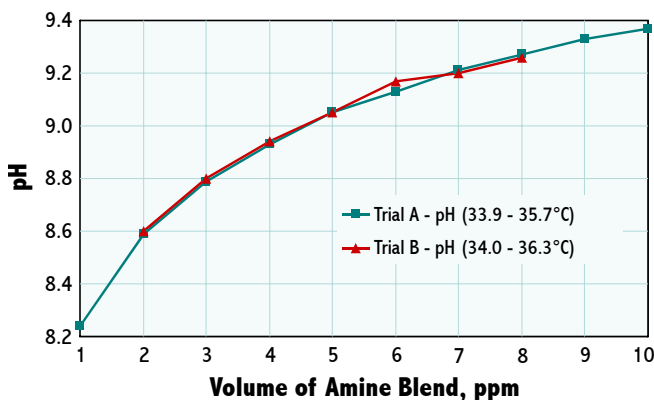
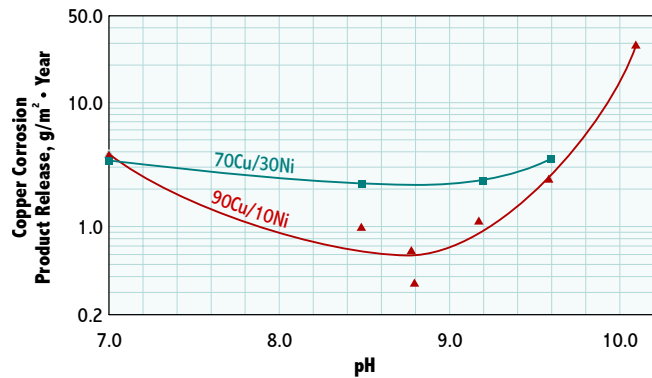


Figure 15 shows the changes in corrosion product transport for two copper alloys exposed to condensate containing ammonia (88). Minimum copper transport for this data occurred around a pH of 8.5-9.2. Other studies have shown a minimum copper transport rate in a reducing environment may occur at slightly higher pH values. Steel corrosion product transport continues to decrease up to pH values of 9.5-10.0. 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 15 - Effect of pH on Copper Transport**

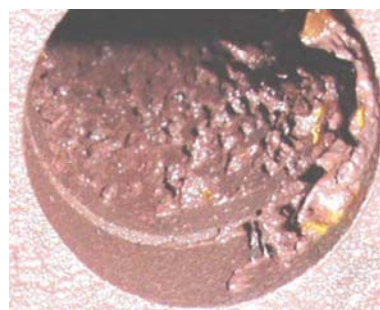


**Dissolved Oxygen and Oxygen Scavengers**

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 16 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. This resulted from a combination of poor deaerator performance and air leakage across the boiler feed pump.

**Figure 16 - Dissolved Oxygen**



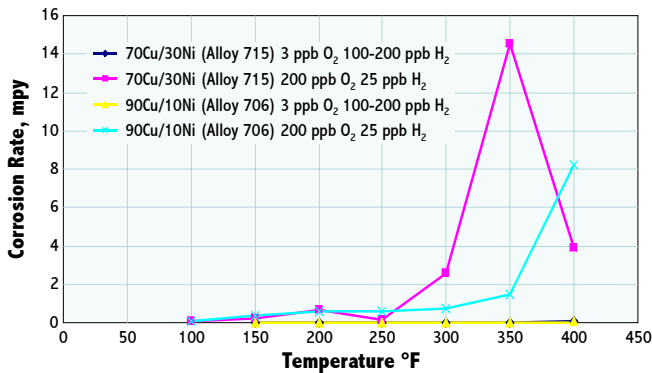
- ◆ Oxygen as O<sub>2</sub> (from air) dissolved in water. Corrodes copper and steel (economizer shown).
- ◆ 1 ppm O<sub>2</sub> = 1 mg/L = 1000 ppb = 1000 µg/L

Figure 17 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.

Normal values and sources of dissolved oxygen in mill water condensate and feedwater are summarized in Figure 18. 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 17 - Dissolved Oxygen Effect on Copper Corrosion**



**Figure 18 - Dissolved Oxygen**

**Normal Values**

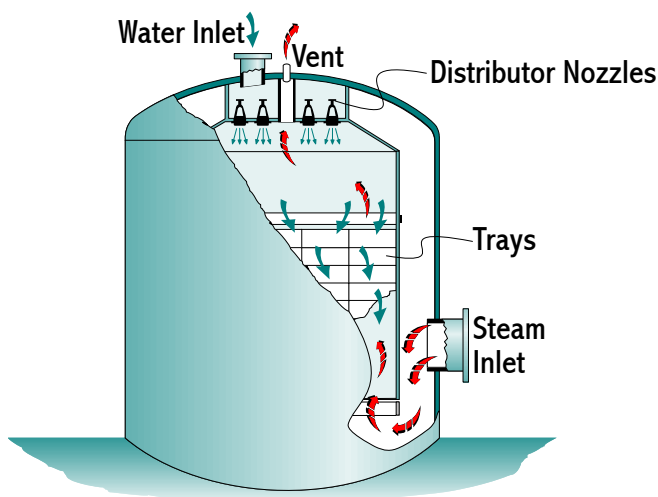
- ◆ Mill Water or Demineralized Water
  - Saturated (8,000 - 14,000 ppb)
- ◆ Condensate: 10 - 100 ppb O<sub>2</sub>
- ◆ Feedwater: <5 - 10 ppb O<sub>2</sub>

**Sources**

- ◆ Air Leaks
  - Where Water Leaks Out, Air Leaks In
- ◆ Mill Water Inleakage
  - 0.1% Raw Water = 8 - 14 ppb O<sub>2</sub>

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 19.

**Figure 19 - 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 20 shows a photograph of a large spray/tray deaerator. Additional details on deaerator operation are presented in the Appendices.

**Figure 20 - Deaerator Spray Nozzles And Trays**



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 in the power industry and may actually be more effective in low temperature systems. As indicated in Figure 21, 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, carbonylhydrazide and other scavengers function as reducing agents which converts red rust (hematite) to black rust (magnetite).

**Figure 21 - Oxygen Scavengers – Carbonylhydrazide Example**

- ◆ Oxygen Scavenging (Reduces Oxygen)
  - Oxygen + Carbonylhydrazide → 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 carbonylhydrazide and other oxygen scavengers is presented in Figure 22.

**Figure 22 - Oxygen Scavenger Feed**

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

For facilities requiring the equivalent of 20-40 ppb of hydrazine (28-56 ppb carbonylhydrazide) or more, consult the appendix on preventive maintenance for monitoring the potential for flow accelerated corrosion (FAC) of feedwater system components. Feedwater line failures from FAC have resulted in fatalities in the power industry.

**Hardness**

Figure 23 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 23 - Hardness in Generation Bank Tube**

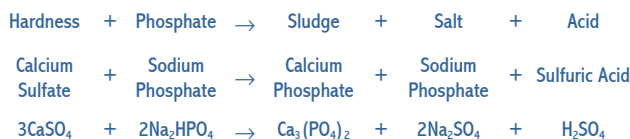


- ◆ Hardness Scale In Generation Bank Tube, Dispersant Treatment
- ◆ Without Dispersants, Gray Mayonnaise Deposits Are In Drums

As indicated in Figure 24, 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 24 - Hardness Definition**

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



Essentially boilers have a zero tolerance for hardness in the feedwater. Any hardness present will precipitate. For lower pressure boilers, dispersants usually are applied to minimize deposition. The ASME consensus guidelines indicate more liberal hardness limits than indicated in Figure 25 (87). Boilers on softened makeup sometimes can tolerate higher levels of hardness.

**Figure 25 - Hardness Limits**

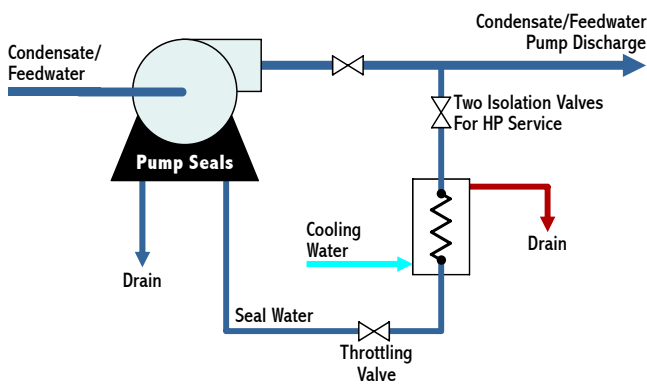
- ◆ Expected Values (ppm CaCO<sub>3</sub>)
  - Feedwater and Turbine Condensate: 0.0
  - Process Condensate 0.0 – Trace
- ◆ Sources
  - Mill Water In Condensate/Feedwater
  - Problem In Makeup Demineralization System

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 (discussed in Appendix B). Figure 26 presents an example of a seal water retrofit which has been implemented at numerous facilities to eliminate a source of hardness contamination.

**Figure 26 - Control of Hardness: Prevent Intrusion**



### Phosphate

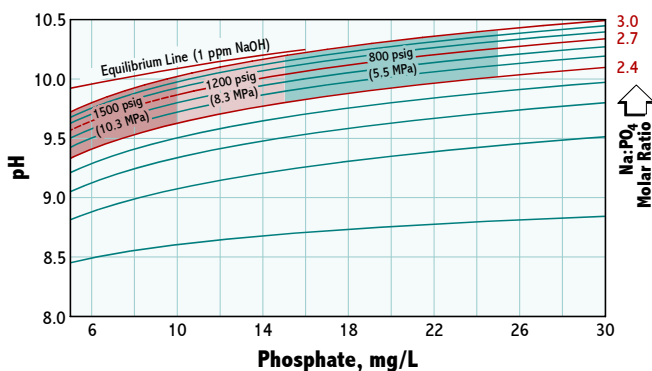
The reasons for phosphate testing and phosphate treatment are summarized in Figure 27. Other treatment programs are discussed in the appendices, but they are less common for modern recovery boilers with demineralized water makeup.

**Figure 27 - Phosphate (PO<sub>4</sub>)**

- ◆ Amount of Sodium Phosphate Dissolved in Boiler Water
- ◆ Units: ppm PO<sub>4</sub> = mg/L PO<sub>4</sub>
- ◆ Purpose:
  - Stabilizes pH
  - Precipitates Hardness as Softer Deposits
  - Backup Indication of Hardness Contamination

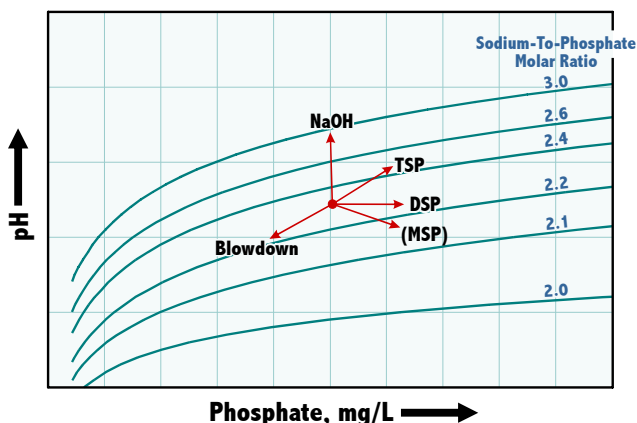
Figure 28 shows the basic control ranges for phosphate treatment for 800 to 1500 psig boilers. Figure 29 shows the effect of trisodium phosphate (TSP), disodium phosphate (DSP), monosodium phosphate (MSP), and sodium hydroxide (NaOH) additions and boiler blowdown on pH and phosphate levels. For stable boiler chemistry, boiler blowdown rates should normally be fixed.

**Figure 28 - Phosphate/pH Control Curves**



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.

**Figure 29 - Phosphate Effect on Boiler Water pH**



### SUMMARY OF STEAM/WATER CYCLE CHEMISTRY

Figures 30 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.

**Figure 30 - Summary: What Should You Know?**

- ◆ Top Chemistry Parameters in Steam/Water Cycle
  - Conductivity  $\mu\text{S}/\text{cm}$
  - pH
  - Dissolved Oxygen, ppb O<sub>2</sub> (and Oxygen Scavengers)
  - Hardness, ppm CaCO<sub>3</sub>
  - Phosphate, ppm PO<sub>4</sub>
- ◆ Steam/Water Cycle, Basic Components
- ◆ Other (See Appendices)

### Appendices

This presentation provided an introduction to a small portion of recovery boiler water treatment. As indicated in Figure 31, nine appendices are included in the written material to provide a more elaborate presentation of steam/water cycle chemistry control in the pulp mill.

**Figure 31 - Appendices**

- ◆ A: Makeup Water Treatment
- ◆ B: Condensate Collection and Treatment
- ◆ C: Feedwater Treatment System
- ◆ D: Boiler Water Treatment
- ◆ E: Steam Purity Considerations
- ◆ F: Additional Chemistry Testing
- ◆ G: Preventive Maintenance
- ◆ H: Personnel Training
- ◆ I: 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 32 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 or each TIP can be obtained individually for a nominal charge (1-4).

Portions of these documents were referenced and discussed during this presentation. These references are good sources of information.

**Figure 32 - For More Information**

- ◆ TAPPI Technical Information Papers
  - **TIP 0416-03** – Water Quality and Monitoring Requirements for Paper Mill Boilers Operating on High Purity Water, 1999
  - **TIP 0416-04** – Design Engineer Decision Tree: Paper Mill Boiler Feedwater, 1999
  - **TIP 0416-05** – Response to Contamination of High Purity Boiler Feedwater, 2000
  - **TIP 0416-06** – Keys to Successful Chemical Cleaning of Boilers, 2000

Many of the recommendations in these chemistry guidelines and discussed in today's presentation and in the appendices 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.

## APPENDIX A: MAKEUP WATER TREATMENT

Constituents dissolved in raw water supplies (typically obtained from wells, rivers, lakes or municipalities) which are of primary concern when preparing this water for makeup to a recovery boiler cycle are calcium, magnesium, salt, organic matter, and silica.

While older mills sometimes used only lime/soda softening or ion exchange softening systems for makeup water treatment, current practice is to prepare demineralized water for all makeup added to recovery boiler cycles - even those operating at low pressures. This approach has the advantages of removing impurities before they can cause harm, and minimizing the problems associated with internal boiler water treatment. The low or moderate pressure units, generally, have cation/anion demineralizers, but mixed-bed demineralizers or equivalent technologies have been used for recovery boilers designed to operate at 6.2-10.3 MPa (900-1500 psig) (10).

TAPPI guidelines TIP 0416-04 provide generalized guidance on makeup system selection (3). However, some of the newer technologies such as Continuous Electrodeionization, used in the power industry have not been incorporated into this guideline. For more in-depth guidance, refer to the references (64). Objectives of makeup water treatment are shown in Figure A-1.

### Figure A-1 - Objectives of Makeup Water Treatment

- ◆ Removal Of Scale-Forming Constituents (Hardness, Silica)
- ◆ Removal Of Dissolved Solids Which Increase Corrosion And Carryover Tendencies (All Other Solids)
- ◆ Treatment Purity Requirements Are Defined By Water Supply And Boiler Design

### Pretreatment

Normally, some pretreatment is needed before raw water can be demineralized - in order to protect the demineralization media (e.g., ion exchange resins, reverse osmosis membranes, etc.) and to maintain the performance of or improve the economics of the makeup water treatment process (Figure A-2). The primary treatment may require clarification or softening plus filtration to reduce hardness (calcium and magnesium) or colloidal matter (silica and organics) or turbidity (suspended silt, clay, etc.). Frequently, treatment with chlorine or other oxidizing biocides is practiced to prevent biofouling, convert metal oxides to less soluble forms, oxidize hydrogen sulfide, and break down organics. Use of oxidant removal techniques usually is applied to protect demineralization media.

### Figure A-2 - Pretreatment for Demineralization

- ◆ Clarification And Filtration
- ◆ Disinfection
  - Chlorine

- Sodium Hypochlorite
- Chlorine Dioxide, Others

### ◆ Oxidant Removal

- Sodium Bisulfite
- Activated Carbon

### ◆ Organic Traps (Figure A-3)

### ◆ Reverse Osmosis (RO)

Organic traps are used as a supplement to remove organics not removed by oxidation (e.g., chlorination), hot-lime softening, or coagulation and filtration. These traps may be as simple as activated carbon, but activated carbon beds have limited life for organic removal. Organic traps usually consist of strong-base anion resin regenerated with either brine or spent caustic left from regeneration of the main anion portion of the demineralizer (Figure A-3). Without pretreatment, organics can severely limit the operation of a demineralizer by fouling the resin beads if the organics are not removed prior to ion exchange (64,65).

### Figure A-3 - Organic Traps

- ◆ Adsorption Process
- ◆ Strong-Base Anion Resin
- ◆ Monitor Organics At Inlet And Outlet
- ◆ Regenerated With Brine

### Demineralization

Demineralization is the process that removes dissolved salts from water. Both the cations (metals or other ions with positive charges) and anions (nonmetal ions with negative charges) which comprise the salts are removed. The process is also called deionization.

The traditional and most common demineralization process is called ion exchange. Ion exchange itself is the reversible exchange of one ion for another between a solution and an ionizable solid (ion exchange resin) without substantially changing the structure of the solid. There are numerous books and papers available which amplify these definitions in many ways, including details of the chemistry involved and the operation of the demineralizer equipment (64,66,67,68).

The demineralization process consists basically of four steps - service (deionization or ion exchange), backwash to cleanse the resin bed of suspended or precipitated solids, regeneration to restore the resin to a usable condition, and rinse to remove excess regenerant and set the bed in preparation for further use (Figure A-4). The deionization or service step is the flowing of water through the cation and anion beds to remove dissolved ions and to replace them with other ions left on the resins by the regeneration process.

**Figure A-4 - Basic Demineralizer Operation**

- ◆ Service (Deionization)
- ◆ Backwash
- ◆ Regeneration
- ◆ Rinse

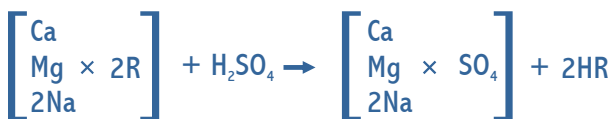
The chemistry involved in demineralization is depicted in Figures A-5 and A-6 for the cation and anion resins, respectively. These simplified drawings show only the ions of greatest concern for recovery boiler water treatment, not every conceivable ion that would be dissolved in every inlet water supply. The cations calcium and magnesium can form heat-insulating deposits on tube surfaces. Excessive amounts of sodium can be of concern since it can form corrosive levels of caustic soda. These cations are split from their salts by the action of the cation resin and become attached to the resin beads. The hydrogen (from the acid regenerant), which replaces them, forms acids with the sulfate and chloride ions remaining in the solution (water). Somewhat similar action occurs with compounds of these cations with bicarbonate or carbonate ions - except that the carbonic acid formed tends to break down to carbon dioxide and water almost immediately.

**Figure A-5 - Reactions Of Strong-Acid Cation Resin With Sulfate And Chloride Salts**

- ◆ Service



- ◆ Regeneration

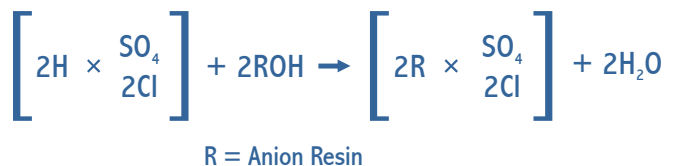


These exchanges continue until the capacity of the resin has dropped to the point where regeneration is needed to restore efficiency of the operation. In some cases, only 40-60% of the resin's theoretical capacity may be used. The cation resin is then backwashed to remove debris and fines (small broken segments of resin beads) and then regenerated with acid. Most commonly in North America, the acid of choice is sulfuric, due to its much lower cost, although hydrochloric acid may be used under special circumstances. Since the natural attraction of the cation resin for different cationic species varies markedly, and is lowest for hydrogen, a surplus of acid is required to obtain a useful degree of regeneration. The acidity of the spent regenerant and rinse water effluents requires neutralization as part of the disposal of the wastes from this process.

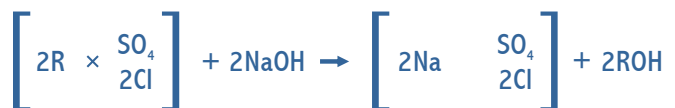
Similar reactions occur with the removal of dissolved anions from solution. Formulae in Figure A-6 show the treatment of water from the cation resin as it undergoes ion exchange with the anion resin. The strong acids (sulfuric and hydrochloric) lose their respective anions as they pass through the resin bed and replace them with hydroxide ions from the resin beads.

**Figure A-6 - Reactions Of Strong-Base Anion Resin With Strong Acids**

- ◆ Service



- ◆ Regeneration



If such ion exchange reactions were perfect through the cation and anion beds, only pure water would emerge from the anion bed, as shown in Figure A-6. As a practical matter, traces of cations (principally sodium) and anions (mostly silica) are present in the final effluent of a two bed (cation-anion) demineralizer train. Once leakage through the anion resin reaches unacceptable levels, the bed is backwashed (to remove any debris and resin fines) and regenerated with a caustic soda solution. This reverse exchange places the anion resin in a condition for further use after rinsing. As in the case of the cation resin, the anion (hydroxide) used for regeneration has little attraction towards the anion resin, so a surplus (generally about twice the theoretical amount) is used to force the reaction. Frequently this caustic waste solution is mixed with the cation (acid) regenerant waste for self-neutralization to reduce the amount of chemicals needed to reach the pH for permissible discharges of wastewater.

While silica (silicon dioxide, SiO<sub>2</sub>) is removed by the anion resin and is frequently called an anion, it is generally not ionized in the bulk solution (some small portion of ionized silicates may be present) and is largely removed from solution by adsorption. Complete removal of silica in one pass through an anion bed is difficult. In some cases, further treatment in a polishing unit - either a mixed-bed or additional anion bed - is used if this contaminant must be reduced further than possible through a single cation-anion train.

Regeneration may be cocurrent (in the same direction of the service flow) or countercurrent (in the opposite direction of the service flow). Conventional cocurrent operation is considered easier to control but does not produce water of

the purity possible with the countercurrent method. For example, effluent silica at 10-50  $\mu\text{g/L}$  is produced with cocurrent designs compared to 1-10  $\mu\text{g/L}$  with countercurrent operation. Similar types of improvement can be obtained in reducing sodium leakage from cation units. Some suppliers claim water purity sufficient for high pressure recovery boiler use by employing countercurrent regeneration with a single train (69).

Several manufacturers furnish what is called split flow regeneration. This type of unit has a vessel with a distributor in the center of the bed to remove regenerants fed simultaneously to the top and bottom of the bed. This design makes it easier to keep a bed in place than with the traditional countercurrent regeneration approach, but gains most of the advantages of having fresh regenerant contact the resin at the point where service water leaves the vessel after being demineralized.

For facilities without suspended matter and consistently low turbidities (i.e.,  $<1$  NTU) in the pretreated water, packed bed demineralizers are commonly used. These are ion exchange vessels that are nearly completely full with resin and are regenerated countercurrently. There are two basic designs: downflow service flow with upflow regeneration, and upflow service flow with downflow regeneration (64).

For greater water purity than available from the effluent of a single train, multiple beds in series may be used, or a mixed-bed unit can follow the first train. Mixed-bed units consist of cation and anion resin beads mixed together in one vessel. In operation, as the water flows past many sequences of cation-anion beads, the result is similar to multiple trains in series. Regeneration is more complicated since the cation and anion resins must be separated as completely as possible before regeneration. Although water purity from a mixed-bed is higher than from the other designs discussed, the difference may not be considered economically desirable when the costs of vessels and regeneration are compared. So long as the demineralization method chosen meets the requirements of the cycle to which the makeup will be added, economic evaluation may determine the final choice.

For both cocurrent and countercurrently regenerated anion units, organic fouling of the anion units may result in significant sodium leakage from the anion units. If this cannot be adequately controlled with alkaline brine cleanings, secondary demineralization or additional pretreatment processes may be required.

### Other Forms Of Demineralization

Where solids in the incoming raw water are high enough (e.g.,  $>200$ - $300$  ppm), a membrane process such as reverse osmosis (RO) usually is used to reduce them; this approach cuts ion exchanger system operating costs. Also, when

followed by cation and anion units, the ion exchangers will function more as polishers and the overall demineralized water quality will be improved - particularly if countercurrent cation and anion units are used. RO units also can drastically reduce organic levels - which reduces organic fouling of the anion units and can result in less organic matter in the treated effluent. While RO units are primarily justified to reduce total dissolved solids levels, sometimes membrane processes are used to reduce organic loading in the influent water (70). Various forms of membrane demineralization, continuous electrodeionization (CEDI), and membrane polishing demineralization which can eliminate the need for any ion exchange units are available (64).

### Typical Types of Makeup Contamination

Trying to convert raw water into demineralized water often is an imperfect process and results in traces of contamination and an occasional upset. This is important because the makeup in a typical pulp and paper mill is 30-60% of the total feedwater flow. The typical types of makeup contamination and effects on the boiler are summarized in Figure A-2.

#### Figure A-7 - Makeup Contamination

##### ◆ Types Of Contamination

- Routine Leakage (Dilute Sodium Hydroxide, Silica)
- Upset: Raw Water (Hardness, Silica, Organic Matter, Salt)
- Upset: Acid Regenerant (Usually Sulfuric or  $\text{H}_2\text{SO}_4$ )
- Upset: Caustic Regenerant (Sodium Hydroxide Or  $\text{NaOH}$ )

##### ◆ Effects Of Makeup Contamination

- Caustic Can Cause Corrosion And Carryover
- Silica Deposits In Turbine And With Hardness In Boiler Tubes
- Hardness And Organic Matter From Adherent Boiler Tube Deposits
- Acid And Salt Cause Corrosion in Boiler And Turbine

Trace contaminants in the makeup are cycled up in the boiler - depending on the percent makeup (makeup/feedwater flow) and the percent boiler blowdown (blowdown/feedwater flow). For example, a mill with 50% makeup and 1% blowdown has 100 cycles of concentration of the feedwater, and 50 cycles of concentration of the makeup. Therefore, a poor demineralization system with 400 ppb as Na of sodium leakage ( $\sim 4.4$   $\mu\text{S/cm}$  of conductivity) would cycle up and contribute 20 ppm of sodium or about 215  $\mu\text{S/cm}$  of conductivity from caustic alkalinity. This assumes zero contamination from the condensate. Significant amounts of treatment chemicals and blowdown (e.g., 3.3%) would be required for this example (based on the feed of just disodium phosphate and maintenance of 25 ppm of phosphate on coordinated phosphate control). However, a high quality demineralized water supply can reduce boiler blowdown and chemical requirements and can greatly simplify steam/water cycle chemistry control. For the example indicated, demineralized water with a conductivity of  $<1.3$   $\mu\text{S/cm}$  would enable 1% blowdown.

The on-line instrumentation shown earlier in Figure 8 (conductivity, sodium and silica) assumes demineralized makeup and is designed to detect most types of chemistry upsets in the makeup plant. Having a specific conductivity activated automatic shutoff valve on the demineralized effluent to storage is a safety feature in a makeup system. In the event of a valve failure in the demineralizer (particularly during a regeneration), the valve can shut off automatically and the demineralized effluent diverted to waste until the source is found and eliminated. Otherwise, a massive acid or caustic leak can contaminate the entire demineralized water storage and cause the Mill to shut down.

## APPENDIX B: CONDENSATE COLLECTION AND TREATMENT

### Condensate Collection System

The actual condensate collection and transfer system can be very complex and can include a series of condensate tanks in series and in parallel. Some, high-energy condensate streams may be routed directly to the deaerator and bypass the condensate polishing system.

Small leaks in black liquor evaporator tubes can result in significant contamination from black liquor. Shutdown of evaporators can result in reverse flow of contaminated steam and result in acidic gasses contaminating normally clean condensate. Also, various process condensers or condensing turbines can have raw water contamination. The automatic conductivity activated dump valves, included in Figure 8 (presented earlier) are standard in most recovery boiler steam/water cycles - particularly for digester and evaporator condensates. The maximum value of the conductivity dump valve should be set at 5  $\mu\text{S}/\text{cm}$  above the normal value (2). This will automatically sewer badly contaminated condensates.

For optimal steam/water cycle chemistry, it is preferred to have all of the condensate cooled through heat recovery (e.g., plate and frame heat exchanger with makeup going to stainless steel makeup storage tank) so that the condensates can be polished before reaching the boiler. Before implementing such design changes, it is necessary to evaluate the deaerator specification and determine if this will reduce deaerator performance.

One feature that has been incorporated into many new boiler designs and retrofitted into older mills was presented in Figure 26. Many older mills have mill cooling water routed to the pump seals for condensate and sometimes boiler feedwater pumps. By taking condensate or feedwater from the pump discharge and routing it through a sample cooler (cooled by mill water), the mill water no longer can introduce hardness and dissolved oxygen to the condensate or feedwater. For water conservation, the pump seals also can be routed to a condensate collection tank.

### Materials Of Construction

In recent years, most new mills have constructed condensate and feedwater components with austenitic stainless steel (usually 304 or 316 alloy) wherever possible. This removes a great deal of copper alloy and carbon steel from the cycle and noticeably reduces the iron and copper found in the boiler (8). Most condensate systems are of such low pressure that only thin-wall stainless pipe need be used, and this frequently reduces construction costs so much that the installed cost of stainless steel is actually less costly than for carbon steel. Many older mills have replaced much of the original preboiler system with stainless, with verifiable reductions in metal loadings in the boiler. There is freedom from outages and/or the high maintenance associated with the older carbon steel systems since the stainless alloys used are relatively immune from attack by the gases (oxygen and carbon dioxide) responsible for most preboiler system corrosion. This type of construction greatly simplifies both feedwater and boiler water treatments.

### Condensate Filtration And Polishing System

The condensates can contain significant amounts of suspended and to a lesser extent dissolved iron and copper oxides. The suspended oxides are removed through filtration. The most common type of condensate treatment was a condensate polisher that functioned as both a filter and an ion exchanger. However, this can be preceded by a separate filter step.

Plain filtration can be provided by sand or anthracite filters, precoat filters, cartridge filters, and electromagnetic filters (EMF). Sand and anthracite filters can contribute to condensate contamination at elevated temperatures. Precoat filters were used extensively in the power industry, but the precoat operation requires more attention than other types of filters. Cartridge filters can require frequent replacement and their use is often restricted by the temperature limitations of the filter media. However, nylon-wound cartridges over a stainless steel core have been found to be satisfactory at temperatures up to 200°F (93°C).

Of the types of filters, the EMF units are most amenable to the paper industry - particularly for high pressure units. Figure B-1 shows one example of a magnetic filter. Magnetic iron oxides are attracted to metal wires or balls during the filtration cycle, and the oxides are periodically backwashed off based on an increase in pressure drop. One ball-type EMF unit that has been in operation since 1996, usually removes at least 40-50% of the iron oxides present and can remove about 20% of the copper (although removal may be much less in the absence of iron oxide). The units are supposed to be more efficient when operated at higher temperatures. While early experience with some of these units was poor, the unit in question has operated with little or no maintenance since 1996. EMF units have been

severely fouled at facilities using filming amines (but this would apply to any type of condensate filtration or polishing equipment) and from fibrous material present in some condensate streams. Usually, EMF units are followed by cation exchangers or mixed beds.

**Figure B-1 - High Gradient Magnetic Filter**

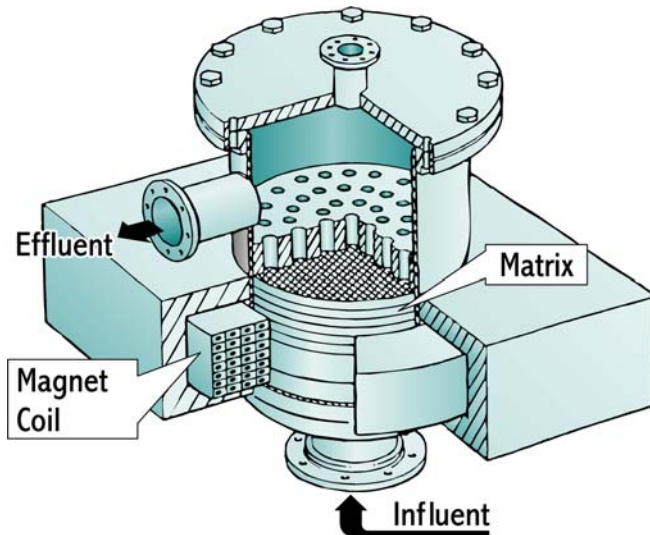
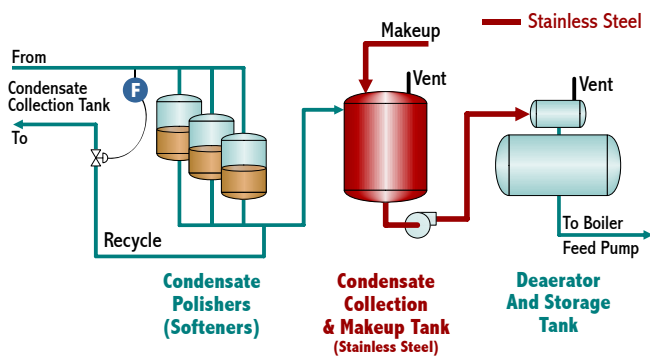


Figure B-2 shows a conventional 3-bed softener system used for condensate polishing. Softeners are vertical cylindrical vessels with a height about twice the diameter and which are half-full of cation exchange resin.

**Figure B-2 - Typical Condensate Polishing System**



Cation exchange resin consists of small plastic (polymerized styrene divinylbenzene) beads that typically are about 0.6-0.7 mm in diameter. The cation exchanger is sized for high flow rates (e.g.,  $\geq 25$  gpm/ft<sup>2</sup> or  $\geq 1.7$  cm/s) that improve its performance as a filter. When the pressure drop across the bed reaches a set value, the resin is backwashed to remove accumulated crud (usually mainly iron oxides with a lesser amount of copper and copper oxides). The recycle loop often is designed to ensure high flow rates in the polisher - for improved filtration.

The polymer chains in the cation resin have sulfonic acid functional groups that attract cations and can be used to exchange various cations. On a microscopic level, the

beads are porous and the water diffuses into the beads and the cations in the water can exchange with the cations on the resin. When most of the exchange sites have been used up, the resin is backwashed to remove suspended matter and then regenerated with a concentrated solution (called a regenerant) of the preferred cations. For makeup demineralizers, acid is used to convert all of the cation exchange sites into the hydrogen form. For cation resin condensate polishers, amine salts or sodium chloride are used. When sodium or amine salts are used, the vessel functions as a softener and removes hardness from the condensate.

When regenerated with sodium chloride it was commonly called a sodium zeolite unit. However, the use of zeolites (minerals with ion exchange properties) for ion exchange now should only be considered for waste treatment, and the use of this term for condensate polishers is discouraged.

If the condensate is frequently contaminated with hardness, sodium chloride is preferred to ensure that anions in the condensate are converted to nonvolatile neutral salts. However, if hardness leakage is rare, amine salt regenerants are preferred. Large amounts of sodium can be eluted from sodium chloride regenerated polishers by amines present in the condensate. For example, up to 800  $\mu\text{g/L}$  of sodium can be released to the boiler by the removal of 3 mg/L of morpholine or cyclohexylamine (9). Sodium elution rates of hundreds of ppb have been noted with polishers with recycle streams around the polisher (to maintain the desired flow rate). At many facilities, amine salt regenerants have replaced sodium chloride for regenerations to reduce the amount of sodium entering the boiler feedwater.

These polishers function mainly as filters for the removal of corrosion products. In fact the flow meter shown in Figure B-2 is designed to maintain a high velocity (e.g., 25-35 gpm/ft<sup>2</sup>) through the beds for improved filtration. The condensate polishers can remove traces of hardness, but resin often is partially fouled with iron oxide and are rather inefficient at softening (i.e., hardness removal).

The vessel and piping downstream of the condensate/demineralized water mixing tank are stainless steel because the high oxygen level makes this mixture corrosive to carbon steel.

Mixed-bed condensate polishers consist of a mixture of cation and anion exchange resin that remove essentially all of the dissolved solids from the condensate. Mixed-bed condensate polishers have been used for 900 psig recovery boilers (10). However, mixed-bed condensate polishers (after an EMF unit) usually only are recommended for consideration if the boiler drum pressure exceeds about 1250 psig (3). They have an absolute maximum allowable operating temperature of 140°F, and they work better below 120°F. Because the condensate temperatures are usually well above these temperatures, the condensate system for the mill has to be specially designed to achieve the desired

temperature. This is easier in facilities with large volumes of turbine condensate (usually at a lower temperature). See TIP 0416-04 for a few suggestions regarding condensate management and treatment. An innovative method of installing mixed-bed condensate polishers in a paper mill by using self-regenerative heat exchangers was described by Kohlvik and Siegmund (10).

Powdered mixed-bed resin systems have been used in the power industry. These are essentially precoat filters that use crushed mixed-bed resin rather than cellulose, diatomaceous earth or other inert materials. While used in some power plants, the systems have limited ion exchange capacity and they are not a good substitute for a mixed-bed polisher.

## Condensate Contaminants

As indicated in Figure B-3, the main type of condensate and feedwater contaminants during normal operation at most mills are corrosion products and much of chemistry testing and monitoring discussions focused on iron and copper control. However, raw water, black liquor and foul condensates also can contribute to harmful contaminants entering the cycle. The raw water concerns are essentially the same as those indicated for makeup contamination. Some mills have reported high color and low pH in boiler water samples resulting from vaporous organic matter entering condensate during flow transients. (e.g., reverse flow of contaminated steam or condensate during batches, water washes, trips, etc.) However, black liquor contamination incidents probably are better understood in terms of the effect on the system and subsequent control.

### Figure B-3 - Condensate/Feedwater Contamination

- ◆ Corrosion Products
  - Main Source of Deposits In Boiler Tubes
  - Main Focus of Chemistry Limits and Treatment Equipment
  - Transport and Deposition is Reduced Not Eliminated
- ◆ Raw Water (Same Concerns As For Makeup Water)
- ◆ Black Liquor (Next Slide)
- ◆ Foul Condensates (Organic Matter and Sulfur Compounds)

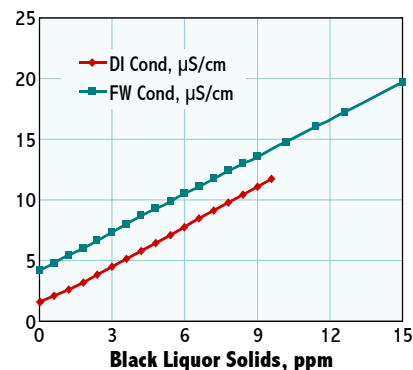
Figure B-4 presents the results of laboratory testing with black liquor added to samples of demineralized (DI) water and feedwater (FW).

The feedwater was treated with the amine blend for which the amine conductivity (Figure 12) and pH (Figure 14) graphs were presented earlier. As indicated in Figure B-4a, the effect of black liquor on conductivity was fairly linear in both types of water. The effect of black liquor on the feedwater pH was considered minor. The test in demineralized water merely shows that it takes very little alkali to significantly change the pH of demineralized water.

It is a recommended practice to set the conductivity dump valves 5  $\mu\text{S}/\text{cm}$  higher than the normal conductivities in the

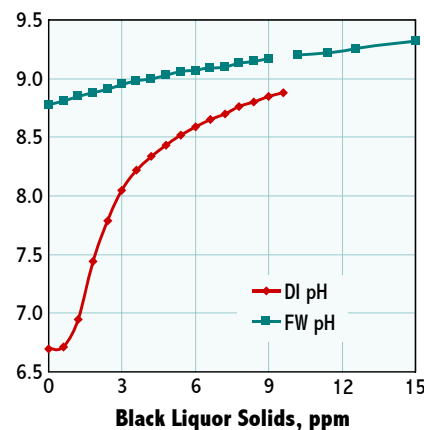
system (2). Unfortunately, mill personnel sometimes have a tendency to increase the setpoints of the various dump valves due to the natural fluctuation in condensate conductivities due to amines. This can delay detection of significant contamination. Based on the graphs in Figure B-4, 5  $\mu\text{S}/\text{cm}$  could correspond to about 5 ppm in the condensate or up to 50 ppm in boiler water based on 60 cycles of concentration, 50% makeup, and assuming only a third of the condensate flow was actually contaminated.

Figure B-4a - Black Liquor Contamination



- ◆ Small Leaks Difficult to Detect in Condensate or Feedwater
- ◆ Conductivity Increases And Automatic Conductivity Dump Valves Are Main Safeguard Against Big Leaks. (Set 5  $\mu\text{S}/\text{cm}$  Over Normal Level).

Figure B-4b - Black Liquor Contamination



- ◆ pH Increases Only Slightly (Red Line) Because Condensate & Feedwater Already Are Alkaline
- ◆ Condensate Turbidity Increases (Can Be More Responsive)
- ◆ Boiler Water Color Increases (Can Be More Responsive)

The conductivity dump valves on the condensate are useful for diverting major black liquor upsets, but they usually are not effective for finding systemic, low-level contamination. For low-level upsets, the color and turbidity monitoring probably are more effective. Figure B-5 summarizes some of the effects on the boiler.

### Figure B-5 - Black Liquor Effects on Boiler

- ◆ Boiler Water Color, Conductivity and pH Increase
- ◆ Adherent Carbon Deposition On Boiler Tubes
- ◆ Boiler Water Foaming and Carryover

Some of the older mills may be more used to upsets of all types including black liquor. If your boiler is operating at a



higher load and/or has not been chemically cleaned in a long time, these practices may no longer be permissible without dire consequences. To better understand some of these concerns, it is suggested to review the effect of deposits in recovery boilers (Appendix D).

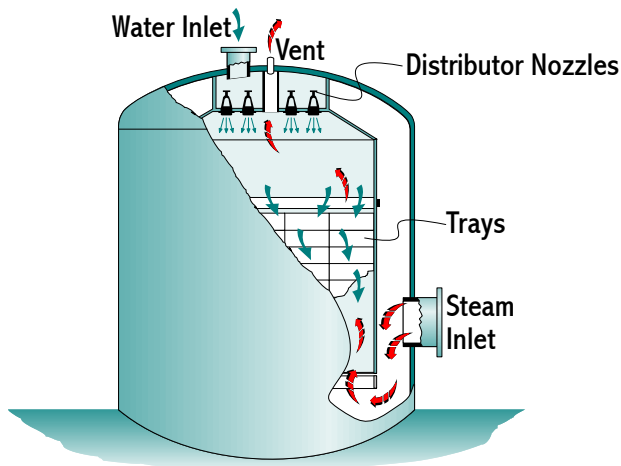
## APPENDIX C: FEEDWATER TREATMENT SYSTEM

### Deaerator

While feedwater sometimes is defined as starting with the boiler feed pump, the deaerator is the start of feedwater treatment. The deaerator is a direct contact steam-fed exchanger that removes dissolved gases from water. The mechanical method of deaeration can reduce dissolved oxygen (the main culprit of corrosion) to a very low level (7 µg/L or less) and substantially lower the concentrations of carbon dioxide and ammonia.

As indicated in Figure C-1, water enters the top inlet water chamber of the deaerator and then discharges through a series of spray valves. This disperses the water into small droplets which greatly increases the surface area which facilitates heat and gas transfer. About 90-95% of the deaeration can occur in this region. The water cascades down across the trays (typically thin pieces of stainless steel with pairs of small lips to retain water). The trays provide a series of shallow pools and cascading water streams which increase the retention time and contact area of the water with the steam.

Figure C-1 - Tray Deaerating Heater



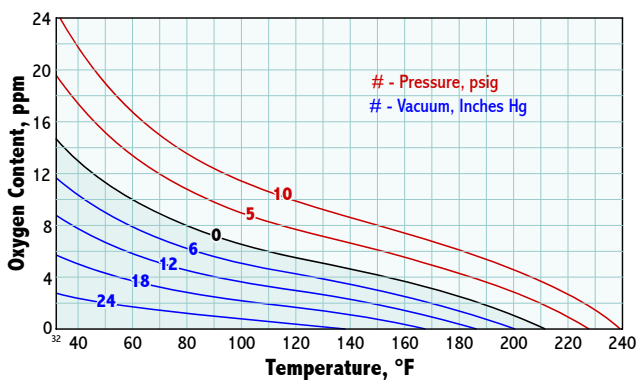
The steam enters the vessel outside of the tray box and flows up through the trays and spray section, counter current to the water flow. A slight excess of steam carries the liberated gases out of the deaerator vent. Figure C-2 presents a photograph of a large deaerator showing the water chamber, spray nozzles and large vent pipes on the top, the stainless steel sides of the tray box, and the cross supports over the trays. The ends of the rectangular trays are just barely visible.

Figure C-2 - Deaerator Spray Nozzles And Trays



As indicated in Figure C-3, the solubility of oxygen in water decreases greatly with increasing temperature. This solubility also is a function of pressure, but the solubility is essentially zero at the saturation temperature.

Figure C-3 - Solubility Of Oxygen In Water Under Saturated Air



The dissolved oxygen liberated from the water is carried away from the water by a countercurrent flow of steam. Since the steam entering the deaerator is relatively free of dissolved oxygen, the partial pressure of oxygen decreases as the water cascades down through the tray box. Therefore, the deaerator functions as a stripper for dissolved gases such as oxygen, nitrogen, carbon dioxide, ammonia, amines, and other volatile materials. However, because of the following dissociation reactions in the water phase, only a portion of the ammonia or carbon dioxide are present as a gas.



Therefore, the removal of carbon dioxide, ammonia, and amine in the deaerator is less efficient (e.g., 25-33%) than oxygen (which generally follows Henry's Law). Figure C-4 summarizes gas removal in the deaerator.

### Figure C-4 - Mechanical Deaeration

- ◆ Solubility Decreases As Temperature Increases
- ◆ Oxygen In Water Also Decreases When Stripped With Steam (i.e., Partial Pressure Of Oxygen In Surrounding Atmosphere Decreases)
- ◆ Removal Efficiency Is High For Oxygen And Nitrogen, Which Behave As Ideal Gases
- ◆ Removal Efficiency Is Lower For Carbon Dioxide And Ammonia

The deaerator is designed to operate under a defined set of operating conditions. The water and steam flow should be fixed to match these conditions. Deviation from these conditions can result in reduced deaerator performance. As indicated in Figure C-5, the only adjustable deaerator operating condition is the level of venting. While large offtake pipes are often present in the deaerator, the vent rate is usually fixed by either an orifice plate or drilled orifices in the vent valves. Supplemental vent valves (startup vents) are opened only during initial operation following startups.

### Figure C-5 - Deaerator Venting

- ◆ Only Operational Control
- ◆ Steady Plume - 30 To 45 Centimeters (12 To 18 Inches) High
- ◆ Excessive Venting Reduces Efficiency
- ◆ Deaerator Testing Must Be At Steady State Without Chemical Addition Upstream

During normal operation, excessive venting wastes steam and thus reduces the deaerator thermal efficiency. Also, high venting rates can sometimes lead to water entrainment which can momentarily block the vent orifice and cause pulsing vent flows. Mr. Poole (see acknowledgments) also performed a series of unpublished tests on a deaerator with a steady vent plume, where reducing the plume height to 1-2 feet (0.3-0.6 meter) resulted in the lowest dissolved oxygen level (in the absence of any chemical reducing agents). However, some deaerators appear to work well with higher vent rates. In a properly operated deaerator, the water temperature in the deaerator storage tank or boiler feed pump discharge should be within 1°C or 2°F of the deaerator saturation temperature, and dissolved oxygen should be below the specified level without oxygen scavenger feed (usually  $\leq 5$  ppb or  $\leq 7$  ppb for modern deaerators).

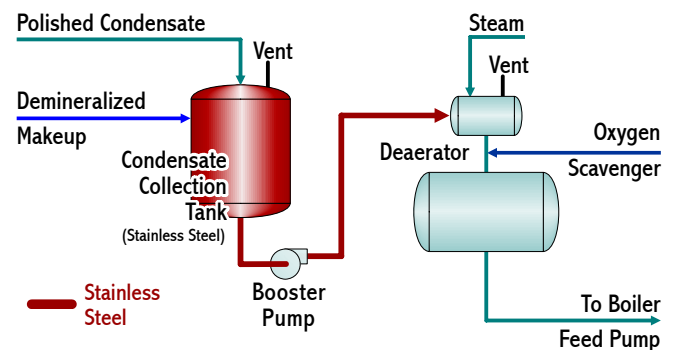
If oxygen scavenger feed rates are elevated, the oxygen scavenger feed should be temporarily removed from service and the deaerator oxygen levels monitored to determine the deaerator performance.

Air present beyond saturation (e.g., from air leaks on makeup or condensate pumps) is sometimes called "free air". In severe cases, excessive amounts of free air may inhibit proper deaeration (11,12).

It has been suggested to combine all condensate and makeup in a premix tank that is adequately vented as shown in Figure C-6 (11). Alternatively, the tank can be fitted with

an air trap to vent off noncondensable gases. This type of design also relieves cyclic stresses in the deaerator due to intermittent hot and cold water flows; these stresses were believed to contribute to deaerator cracking (13). In unpublished reports, it has been indicated that cyclic temperatures also have caused stainless steel inlet chambers in deaerators to shatter. However, in some deaerators, both hot and cold streams are successfully introduced through separate or segregated spray headers.

Figure C-6 - Recommended Deaerator Feed



When implementing heat recovery projects, it is advised to evaluate the effect on the range of deaerator feed flows and temperatures (minimum, average, and maximum) on the deaerator performance. Typically, the deaerator supply temperature should be at least 30-40°F (17-22°C) less than the deaerator operating temperature. Increases of the inlet temperature decrease the steam demand and steam flow entering the bottom of the tray box. This reduces the stripping action and can reduce deaerator performance. Deaerators manufacturers report that lower temperature differentials can be accommodated at the deaerator design stage by increasing the height of the tray stack.

### Oxygen Scavenger Addition

Oxygen scavengers are reducing agents that usually are applied to the drop leg from the heater section to the deaerator storage tank to reduce residual dissolved oxygen in the deaerator outlet. Minimizing dissolved oxygen levels in Recovery Boiler feedwater and in the steam supplied to copper heat exchangers generally is accepted by the pulp and paper industry to avoid economizer corrosion and minimize copper corrosion in the condensate system (2).

Figure 17 (presented in body of paper), which was calculated from data presented by Brush and Pearl, presents the effect of dissolved oxygen on the corrosion of copper alloys at different oxygen levels (14). Corrosion was negligible with 3 ppb of oxygen and an excess of reducing agent (100-200 ppb hydrogen) and corrosion was very high with 200 ppb of dissolved oxygen.

Oxygen reacts with metallic copper to form oxides that are more soluble in aqueous solutions, while carbon dioxide

either aids in complexing and dissolving the copper directly or assists corrosion by reducing the pH (15). Ammonia and some amines complex cupric oxide and hold it in solution until it reaches the feedwater or the boiler; this action speeds up the copper corrosion process. Since temperature is a major rate controlling factor in the dissolution of copper, it is not surprising that copper is more readily picked up from heat transfer surfaces where tubes or plates are exposed to steam, such as copper tube dryers or feedwater heaters. The major contributors to the pickup of copper are low pH, high dissolved oxygen, dissolved carbon dioxide and dissolved ammonia. With the exception of ammonia, all of these factors also enhance iron corrosion.

The effect of dissolved oxygen on carbon steel is more complex and is dependent on the purity of the water present. Figure C-7 presents a compilation of corrosion data from various sources that shows the range of corrosion that can be experienced at different oxygen levels (16,17). Excessive levels of strong reducing agents (fed as oxygen scavengers) contributes to flow accelerated corrosion (FAC) of steel surfaces. Dissolved oxygen levels below 2 ppb with highly reducing conditions resulted in the failure of a feedwater line in a nuclear plant in the 1980's. Since that time, similar attack has been noted in numerous other power plants. In such cases, higher dissolved oxygen and/or lower reducing agent levels are required to avoid damage to steel surfaces and minimize corrosion product transport. While it could not be accommodated on Figure C-7, a much lower steel corrosion rate was obtained with 22.5 ppb oxygen (16). However, dissolved oxygen levels above a few ppb generally are only considered in high purity, all-steel, power plant steam/water cycles. Therefore, the only option for susceptible mixed-metallurgy paper mills is to minimize both dissolved oxygen and the use of a small excess of oxygen scavenger.

**Figure C-7 - Erosion/Corrosion At Elevated Oxygen (O<sub>2</sub>) Levels**

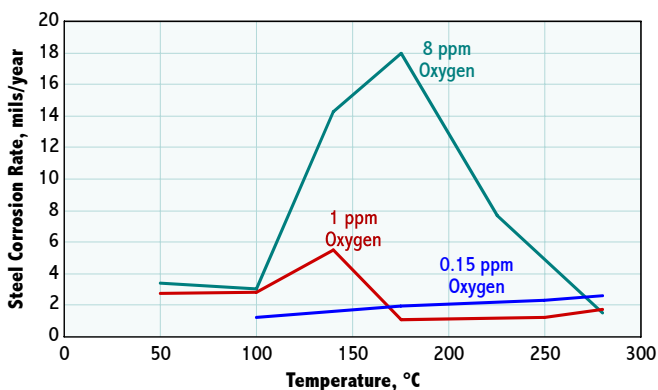


Figure C-8 summarizes the experience of an economizer for a 450 psig Recovery Boiler that failed in less than six years due to a poorly operated deaerator and insufficient oxygen scavenger (18). Figure 16 in the main body of the paper

shows a recent (2005) incident of oxygen pitting which occurred in the economizer inlet of a 700 psig recovery boiler after less than a decade of operation. Deaerator storage tanks for recovery boilers also have suffered severe oxygen pitting.

**Figure C-8 - In-Service Corrosion Of Recovery Boiler Economizer**

- ◆ 450 psig Black Liquor Recovery Boiler
- ◆ Uncontrolled Dissolved Oxygen
- ◆ Economizer Failed In 5.5 Years
- ◆ Failure Analysis Indicated Tubercles From Oxygen Pitting
- ◆ Based On Case I In Dennis A. Frey, "Case Histories Of Corrosion In Industrial Boilers" Corrosion 80, Paper 77, 1980.

The effect of feedwater dissolved oxygen on boiler tube corrosion may be more complex. Most of the dissolved oxygen entering with the feedwater will be removed with the steam leaving the steam drum and only a small proportion of the dissolved oxygen will actually flow down the downcomers. Holmes and Mann indicated that oxygen pitting does not occur on boiler tubes during operation (19). However, early studies indicated that the addition of sodium sulfite to reduce feedwater oxygen reduced the frequency of boiler tube failures (20). Other studies by Mann and by Kimmel on test boilers indicated that dissolved oxygen may accelerate and oxygen scavengers may inhibit other corrosion mechanisms in boiler tubes (21,22).

The first oxygen scavenger widely used in North America was sodium sulfite, a white, alkaline solid. Sodium sulfite reacts with dissolved oxygen to form sodium sulfate. Sodium sulfite still is the fastest oxygen scavenger and is recommended for low pressure HVAC boilers and 450 psig or 600 psig boilers with softened makeup and free caustic alkalinity in the boiler water. It also has been recommended for boilers operating around 700 psig (4.9 MPa) where the deaerator performance is very poor.

However, sodium sulfite is a solid, nonvolatile chemical that cannot be used in facilities that use feedwater for attemperation. If the unit uses feedwater for steam attemperation, solid chemicals cannot be used in the feedwater without potential damage to the superheater and turbine. Also, sodium sulfite will decompose and release acid gases containing sulfur (believed to be primarily H<sub>2</sub>S and SO<sub>2</sub>) to the steam. As steam is condensed, these gases dissolve and form acids in the condensate. Early static bomb tests by Taff at pH values of 9.5-11.0 indicated that sulfite would not decompose below 850 psig (5.9 MPa) (23). Problems with sulfite decomposition in boilers operated with free caustic alkalinity were mainly apparent at pressures above 1050 psig (7.2 MPa), and sulfite decomposition increased with decreasing pH values (24). However, sulfite decomposition has been detected in operating boilers down to 600-655 psig (4.1-4.5 KPa) (25). For these reasons, sodium

sulfite has been largely replaced with volatile materials which can scavenge oxygen, passivate metal, and not add solids to the boiler water or acids to the condensate system.

Hydrazine was the first and is still considered one of the best of the all-volatile reducing agents or oxygen scavengers by the power industry. The technology was brought from Europe to the United States around 1951 and by 1954 twenty two power plants were using hydrazine (20). As indicated in Figure 16 (presented earlier), the products of reaction formed are nitrogen (an inert gas) and water, neither of which will interfere with use of feedwater for attemperation.

The drawbacks to its use are the slowness of the hydrazine/oxygen reaction at temperatures much below 200°C (400°F) and the fact that it is now classified as a possible carcinogen. The slow direct reaction with oxygen is offset by the passivating action of hydrazine on metal -which takes place quite rapidly at temperatures only slightly above ambient. Passivation consists of the formation of a protective layer that inhibits further corrosion.

Any ingress of dissolved oxygen is spent on reconverting the oxides or metal to their respective more highly oxidized states. More hydrazine from the continuous feed again reduces the oxides to maintain passive conditions.

Hydrazine was almost universally implemented from the 1950's until the mid 1970's when studies on laboratory animals indicated hydrazine was a possible carcinogen. The old timers said that hydrazine was carried around in buckets at a lot of plants. Following the classification as a suspect carcinogen, handling requirements became much more strict. Currently, it is usually fed from sealed systems that eliminate or minimize human contact. It has continued to be used by many power plants in the United States, and we have heard of no case of human cancer resulting from the use of hydrazine. However, the writer recalls hearing one story of someone having an allergic reaction (would break out in hives) upon direct contact with hydrazine.

As a result of the concerns with hydrazine, a number of hydrazine substitutes are available. Carbohydrazide and diethylhydroxylamine (DEHA) were two of the first hydrazine replacement compounds in the U.S. and their patents are no longer in effect. Both are reported to be passivators and oxygen scavengers. However, as with hydrazine, the passivation effect may be more significant. The reactions of carbohydrazide with oxygen and metal oxides may be found in the literature (26).

Chemical suppliers have introduced many proprietary compounds for use as volatile oxygen scavengers and metal passivators. These materials are offered as noncarcinogenic and are claimed to possess chemical advantages over hydrazine. However, caution is advised, because hydroquinone,

one of the hydrazine substitutes, was later classified as a carcinogen in Germany (27).

For some of these hydrazine substitutes, manufacturers have produced test results showing faster reaction times with oxygen at low temperatures and showing good passivation with metals. However, some of the newer compounds function more as passivators, do not necessarily scavenge the oxygen, and readily decompose in the feedwater. Some vendors are tending to refer to them as passivators rather than oxygen scavengers. However, if the oxygen is not adequately removed from the feedwater and steam, and the scavenger is decomposed, corrosion in copper heat exchangers receiving the steam could be of concern.

### Amine Addition for Feedwater pH Control

With all other factors being equal (temperature, oxygen ammonia, flow rate, etc.), the degree and rate of attack on copper and iron alloy components can be reduced by controlling the pH. Experience has shown that maintaining pH near 9.0 in a mixed metal system offers maximum protection to the metals. A higher pH would give some additional protection to steel, but - since pH must be controlled by ammonia or some other volatile, alkaline material - raising the pH much above this value can increase the attack on copper alloys (especially brasses). The importance of pH control in condensate and feedwater is summarized in Figure C-9.

Concentrations of three different, commonly used materials needed to maintain pH 9.0 are as follows:

- Ammonia 0.2 ppm
- Cyclohexylamine 1.0 ppm
- Morpholine 4.0 ppm

#### Figure C-9 - Importance Of pH In Condensate/Feedwater System

- ◆ High pH Reduces Iron Transport (Minimized 9.5-10.0)
- ◆ High pH (>9.0-9.3) Increases Copper Transport
- ◆ Typical pH Target Of 8.8-9.2 In Paper Mill Condensate/Feedwater Is A Compromise

These values assume no carbon dioxide is present; if some of this gas is dissolved in the water, enough of the amine used to neutralize carbon dioxide would have to be added plus a surplus to raise the pH to 9.0. Since more morpholine or cyclohexylamine than ammonia is required to neutralize carbon dioxide, the final amounts added would be even more disproportionate. Generally, blends of high and low volatility amines are required to provide the desired pH elevation throughout the steam/condensate system.

## Overview of Feedwater Treatment Considerations

Most deposition currently found in recovery boiler water-wall tubes consists of metal oxides, primarily iron and copper which originate in the condensate/feedwater system. Mills having makeup water facilities producing water with less purity than achieved by demineralization still may have buildups of hardness salts, but today such deposition is not generally prevalent. Of course, any boiler cycle can experience sudden major episodes of contamination, as may result from failures in equipment handling black liquor, inleakage from the bleach plant, or introduction of large quantities of untreated mill water. These contaminants can cause precipitation of hardness, silica, and organic matter onto tube surfaces - the amount of which depends on the extent and length of time of the contaminant ingress.

## APPENDIX D: BOILER WATER TREATMENT

As indicated in Figure D-1, feedwater flows through the economizer to the steam drum. Modern recovery boilers can have several large economizer sections. In the steam drum, feedwater and boiler water flow down the downcomer tubes in the generation bank and down the downcomer pipes from the mud drum to the lower headers and screen wall headers. Some boilers do not have downcomer tubes or mud drums and all of the water flows down downcomer pipes to supply various headers. Boiler water flows up the waterwall tubes, screen tubes and generation bank riser tubes. Steam is generated in these areas. When the steam reaches the steam drum, the steam/water mixture may be about 70-75% by volume (28). Actual proportions vary depending on the boiler pressure and steaming rate.

**Figure D-1 - Recovery Boiler Overview**

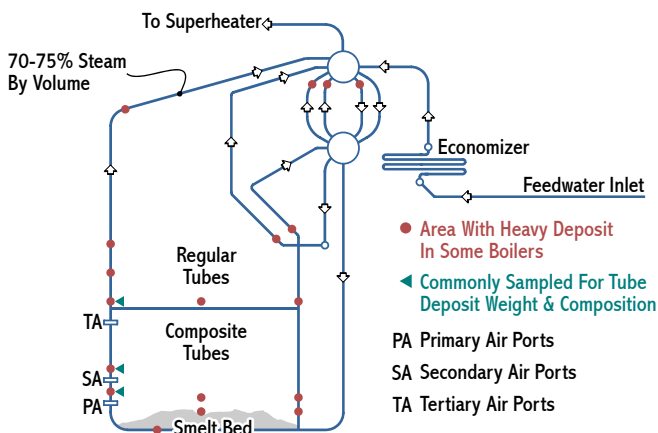


Figure D-1 also shows the areas where heavy deposits have been found in recovery boilers and common locations for routine (every one to three years) tube sampling. Traditionally, these were around the primary and secondary air ports. However, sometimes, units with composite tubes are sampled in the carbon steel at the composite tube to plain

carbon steel transition. Heavy deposits also have been found further up the waterwalls and in the sloped roof, nose, screen, and floor tubes and in tubes in the generation bank.

## Boiler Tube Temperatures

The following table presents the estimated temperatures of water and tube metal in Recovery Boilers. The water temperature is fixed by the operating pressure of the boiler. While there have been lower pressure recovery boilers (3.1 MPa, 450 psig), typically they range from 4.1 to 10.3 MPa (600 to 1500 psig) and operate with heat fluxes up to 126,000-189,000 W/m<sup>2</sup> (40,000-60,000 BTU/hr/ft<sup>2</sup>).

**Figure D-2 - Recovery Boiler Pressures And Temperatures**

Boiler Pressure kPa (psig)	Saturation Temperature °C (°F)	Max. Clean Tube Temperature °C (°F)
4,135 (600)	254 (489)	265-295 (509-563)
6,200 (900)	279 (534)	290-320 (554-610)
8,270 (1,200)	298 (569)	310-340 (590-640)
10,340 (1,500)	314 (597)	330-360 (626-680)

### ◆ Gas-Side Metal Temperatures With 126,000-189,000 W/m<sup>2</sup> (40,000-60,000 Btu/ft<sup>2</sup>/hr) Heat Flux

During operation, the outer diameter (OD) surface of the tubes are estimated to be up to 11-46°C (20-83°F) hotter than the boiler water. The last column in the table presents estimates of the maximum metal temperatures based on values in the literature and the writer's estimates. Metal temperatures increase with increasing boiler pressure, increasing heat flux, increasing wall thickness, and decreasing tube diameter. Literature sources are discussed in the following paragraph.

Past thermocouple measurements indicate fireside surfaces (Outer diameter, OD) of waterwall tubes to be up to 28°C (50°F) above the saturation temperature with a heat flux of 189,000 W/m<sup>2</sup> (60,000 BTU/hr/ft<sup>2</sup>) (29). However, errors in tube metal temperature measurements were estimated to be 8-11°C (15-20°F), and the maximum temperatures in the preceding table for 900-1500 psig boilers were based on estimates provided by Plumley and correspond to a temperature rise of up to 39-46°C (71-83°F) for a heat flux of 189,000 W/m<sup>2</sup> (60,000 BTU/hr/ft<sup>2</sup>) (29). Walsh (25°C, 45°F) and Green (15-30°C, 27-54°F) have indicated the maximum temperature rise from the tube OD to the water to be at intermediate values for recovery boilers (28,30). The average heat flux in a recovery boiler can be about half the maximum heat flux in the lower furnace (29). Modification of the boiler design for new or retrofitted boilers or changes in liquor, or combustion process could further increase heat transfer rates and resultant tube metal temperatures from values listed herein.

### Effect of Temperature on Fireside Corrosion

Plumley and Rocznik noted that areas of carbon steel waterwall tubes with thinning were associated with internal deposition and overheating of tube metal (31). Other investigations have found that buildup of scale on the insides of waterwall tubes has caused high temperatures and rapid corrosion of metal on the firesides of tubes (30,32,33). This damage typically occurs in the high heat areas in the lower furnace. The corrosion of carbon steel in the lower furnace of Recovery Boilers accelerates greatly above 330°C (625°F) (31,34). While boilers with composite tubes may require much higher temperatures before experiencing overheating or fireside corrosion, the upper furnace still contains carbon steel. Also, waterside deposits throughout the furnace can still contribute to waterside corrosion of carbon steel and composite tubes (stainless steel is only on the outside).

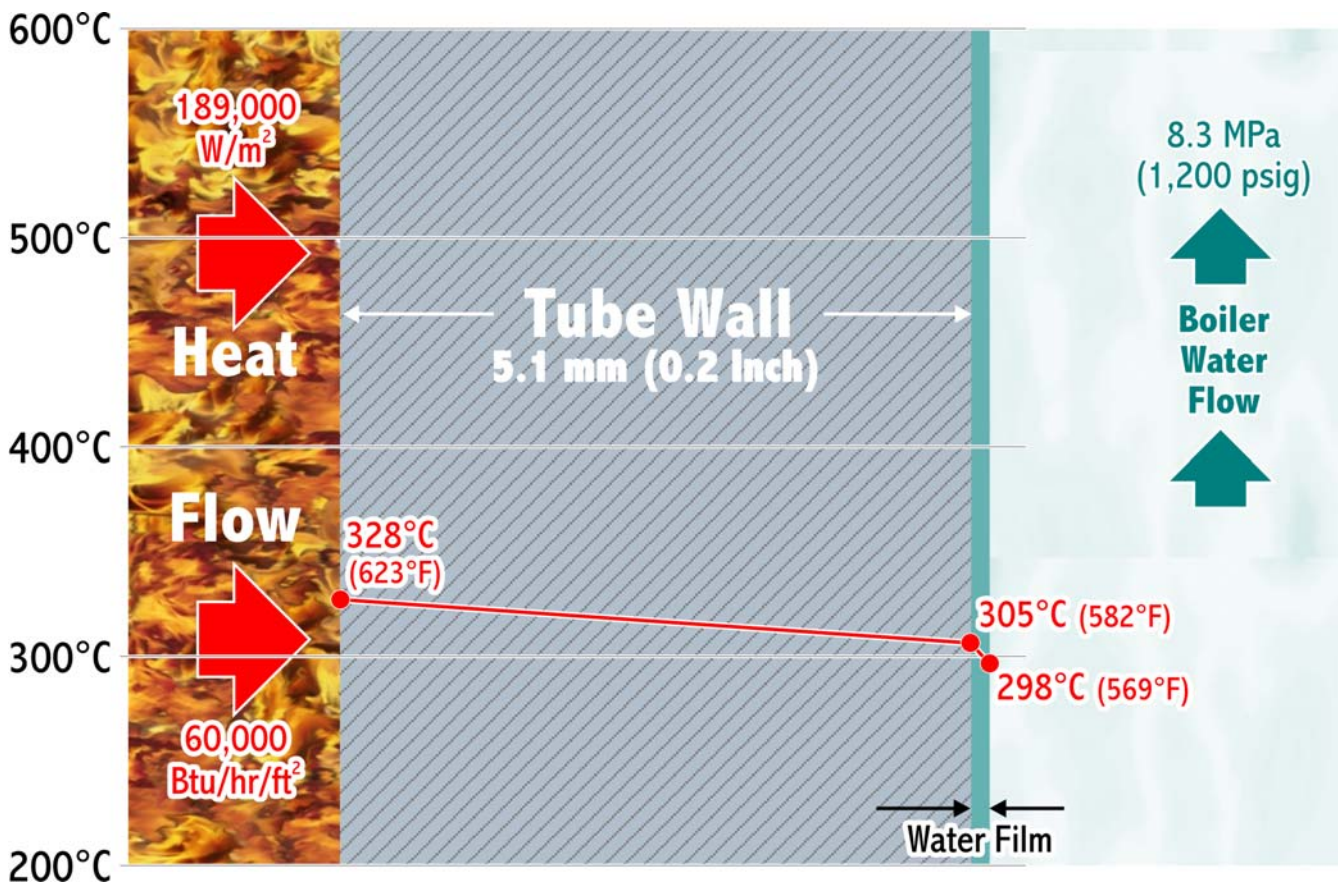
### Effect of Waterside Deposits on Tube Temperatures

Figures D-3 and D-4 depict side views of heat transfer through the fireside surfaces of clean and dirty waterwall tubes, respectively. The boiler furnace is on the left, heat flows from left to right, and a steam/water mixture is flowing up the inside of the waterwall tube.

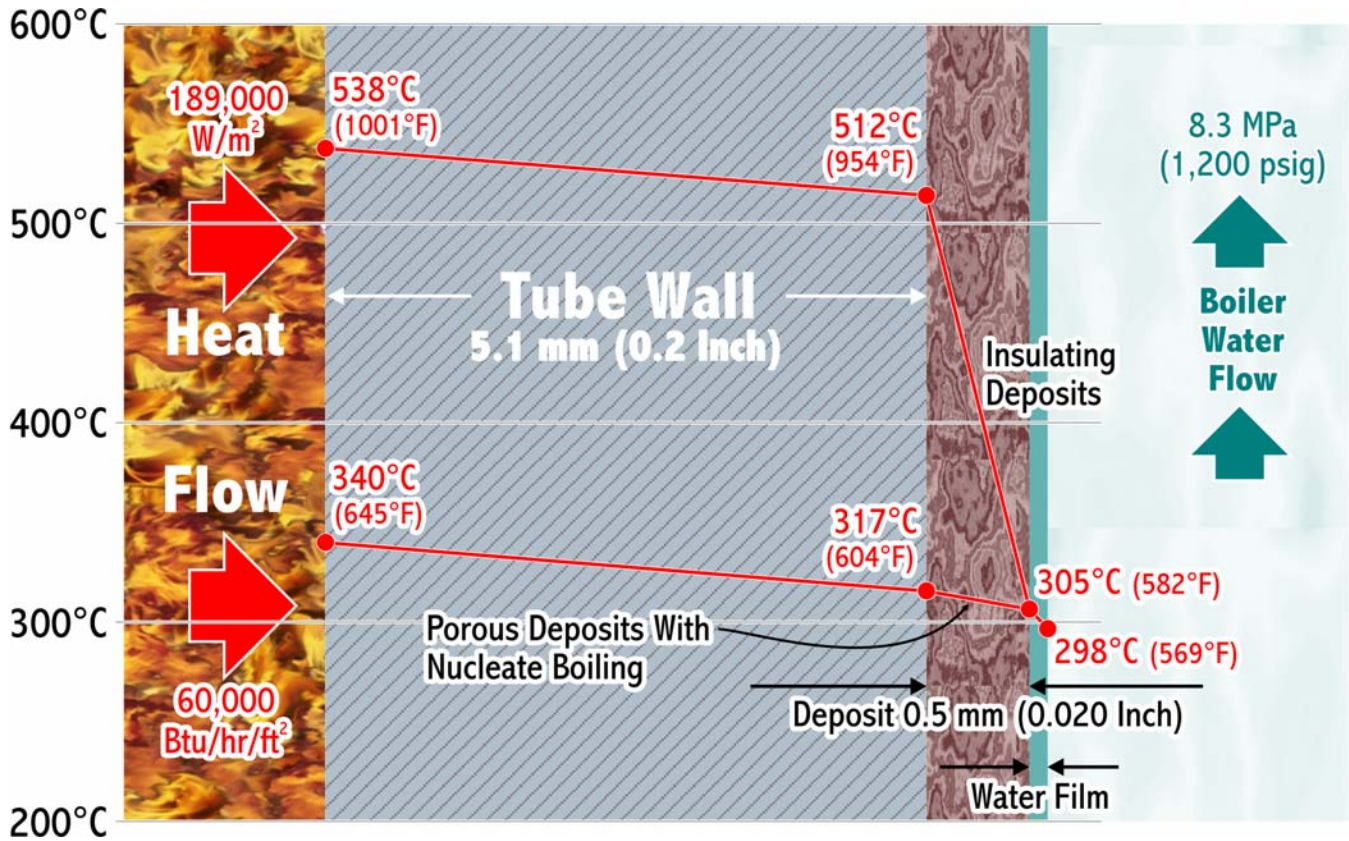
On the clean tube, the only temperature losses are due to the tube wall and convective losses at the tube metal/water interface. The resultant fireside temperature of 328°C (623°F) is within temperature limits for carbon steel and, therefore, will not harm the metal wall.

If an insulating (0.59 W/m/°K or 0.34 BTU/hr/ft/°F) scale 0.5 mm (0.020 inch) thick forms on the hot waterside of the tube, the temperature loss due to this scale added to the interface and tube wall temperature losses may cause the fireside temperature of the tube to rise to 538°C (1001°F). Estimates were performed based on the methods and deposit thermal conductivity suggested by French, although steel thermal conductivities were estimated from curves from Stultz and Kitto (35,36). However, in the case of more porous magnetite scales with boiling under the deposits, the effective thermal conductivity can sometimes be much higher (e.g., 10 W/m/°K or 5.8 BTU/hr/ft/°F) (37). In such an event, the deposits would increase the temperatures of the tube OD and ID by only about 12°C (22°F) rather than 207°C (372°F). The resultant fireside temperature (340°C, 645°F) would contribute to fireside corrosion (as well as waterside concentration mechanisms discussed later), but are well below the temperatures required for overheating. Since overheating of waterwall tubes is rare, it is expected that the temperatures are probably below the upper line in Figure D-4 for most tube deposits.

Figure D-3 - Heat Transfer - Clean Tube



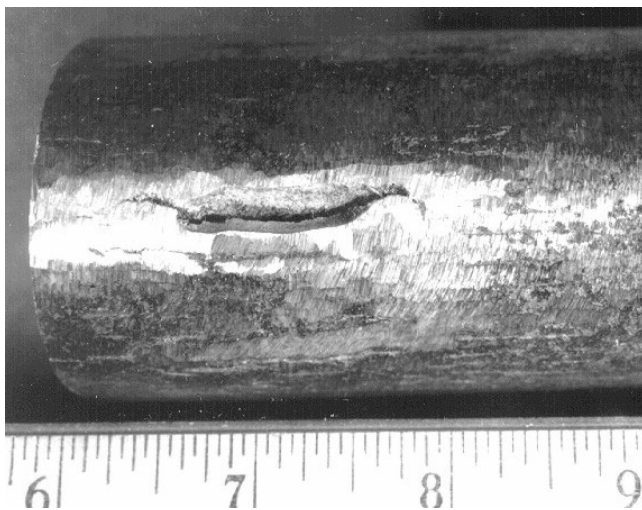
**Figure D-4 - Heat Transfer - Dirty Tube**



**Overheating Failures**

There are two general classes of overheating failures: long-term and short-term overheating. Figure D-5 presents a long-term failure.

**Figure D-5 - Example Of A Long-Term Overheating Failure**

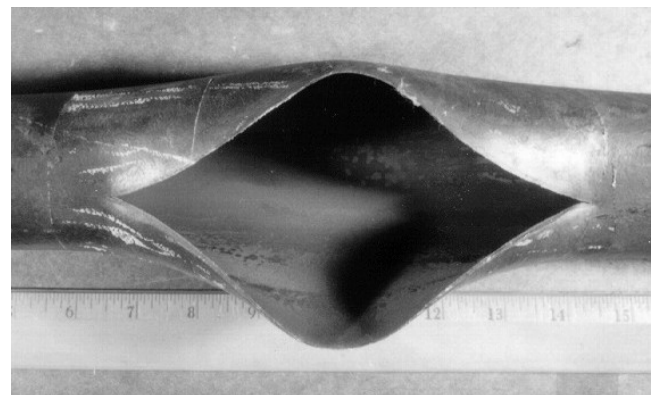


This tube has been held at an elevated temperature for a long time (usually years) and the crystal structure has gradually become brittle. Eventually, the steel is weakened

enough that it can no longer hold the internal pressure. It starts to expand, but quickly cracks because it is brittle. Long-term overheating failures have thick-lips at the failure and may result from temperatures as low as 400-425°C (750-800°F), although it usually is associated with temperatures in excess of 425°C [800°F].

The thin-lipped failure in Figure D-6 is an example of short-term overheating.

**Figure D-6 - Example Of A Short-Term Overheating Failure**



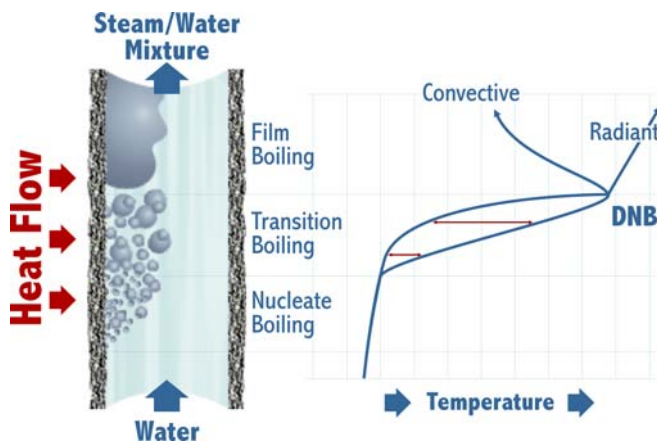
Plain carbon steel (e.g., SA 210-A1) loses about a quarter, two-thirds and ninety percent of its rated strength at temperatures of 427°C (800°F), 482°C (900°F), and 538°C

(1000°F) (35). In short term overheating, the temperature increases to the point where the strength of the tube is incapable of retaining the pressure. However, since the tube has only been at a high temperature for a short period of time, it is still ductile. Therefore, the tube blows up like a balloon until it fails. If an object (e.g., outage debris) or a mass of sludge suddenly obstructs and starves a waterwall tube of water, this type of failure usually will result.

### Departure from Nucleate Boiling

Boilers are designed to transfer heat and generate steam through nucleate boiling. As indicated in the bottom of Figure D-7, this involves the formation of many tiny bubbles forming throughout the metal surface. The tiny bubbles release, the boiler water washes the surface and another bubble forms.

Figure D-7 - Departure From Nucleate Boiling



As the heat flux is increased, a phenomenon known as Departure From Nucleate Boiling (DNB) can occur where the bubbles interfere with heat transfer and the tube temperature rises because heat transfer is less efficient. Operation beyond DNB initially can result in cyclic temperatures of 10-20°F in intervals of seconds or more due to unstable or transition boiling (38). Further increases in the heat transfer can cause the bubbles to coalesce and essentially steam blanket the tube (38). As indicated in Figure D-7, the temperature can drop slightly or continue to increase - depending on the dominant type of the fireside heat transfer (convective or radiant). The tube wall will usually fail within a relatively short time unless heat flux (i.e., load) and temperatures are reduced (38). Boilers are designed, operated, and chemically cleaned to operate with nucleate boiling below DNB.

To prevent DNB in Recovery Boilers, the volume of steam in the tube must be kept below about 70-75% (28). Similar volumetric steam fractions (65-80%) were cited years ago for boiler design (39). According to the steam tables, steam volumes of 70-75% correspond to maximum weight fractions of steam (i.e., steam quality) in the waterwall tubes of 6-7%, 9-12%, and 17-20% for 4.1, 6.2, and 10.3 MPa (600, 900, and 1500 psig) boilers, respectively (40). Boiler manufacturers use the circulation ratio, which is the weight ratio of the mass of boiler water to the mass of steam leaving a waterwall tube, in the boiler design. The corresponding water flows to waterwall tubes should be 13.3-16.9, 8.7-10.9, and 4.9-6.0 times the steam flow for these pressure boilers, respectively. Boilers modified to increase liquor firing or steaming capacity need to ensure sufficient water circulation to avoid DNB.

### Effect of Heat Flux on Deposition

The preceding discussion has demonstrated that the tube metal is hotter than the boiler water. In addition to overheating and fireside corrosion concerns, hot waterside surfaces can lead to deposition and corrosion on the waterside surfaces. Holmes and Mann reported of a 1960 study by Mankina that studied the effect of heat flux on the rate of iron and copper oxide deposition (19). Oxide deposition increased with the square of the heat flux (19). More recent studies have shown different relationships between heat flux and deposition rates (93,94).

### Effect of Heat Flux on Concentration

Hot metal surfaces on the waterside of a tube concentrate dissolved and suspended matter in the boiler water. Envision a hot frying pan heating on the stove. You check to see if it is hot enough by throwing some tap water on the frying pan and watching how fast it evaporates. If you do this enough, you will see a white film form on the metal surface. These are the dissolved solids left by the evaporating water.

The same sort of mechanism occurs in boiler tubes. The tube is always hotter than the water, and solids from the evaporating boiler water will concentrate along the tube surface. The degree of concentration depends on the rate of steam generation and water flow up the tube.

There is a classic theory, called "wick boiling", that says the water diffuses through pores in the deposit to the tube surface where the steam is generated. The steam is then released through a "chimney" in the deposits, much like the way lava is released from a volcano. Figure D-8 presents wick boiling.



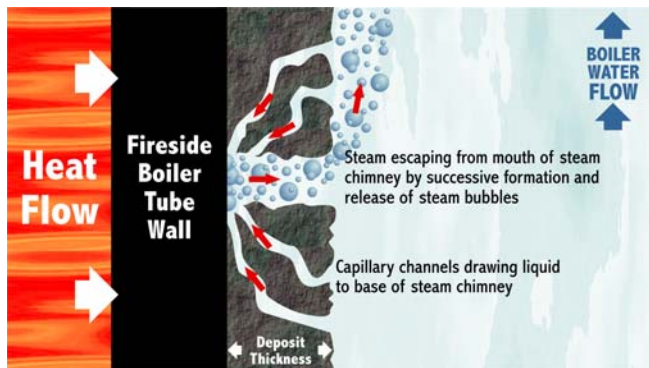
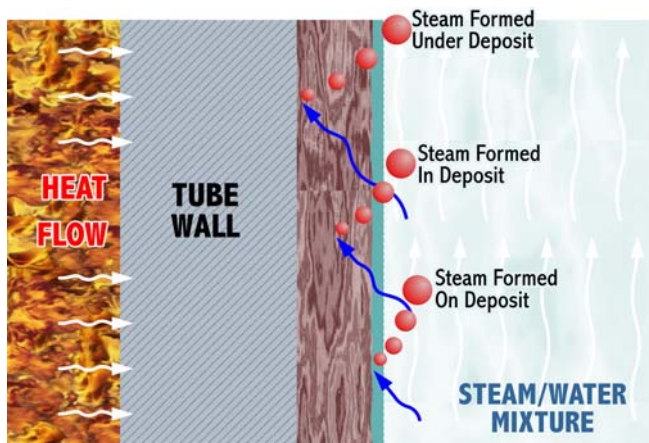
**Figure D-8 - Wick Boiling**

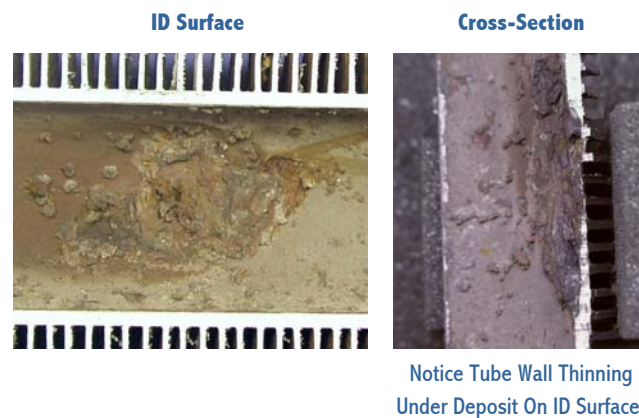
Figure D-9 presents an extension of this concept in that it suggests that steam formation can occur on, in, and under deposits. Thus, during operation some water may evaporate and concentrate suspended and dissolved solids at the deposit surface. Some of the boiler water will diffuse into the deposits and evaporate, and some will penetrate to the tube surface. This should develop a concentration gradient from the boiler water to the tube surface. Also, along the way, some of the suspended matter could deposit on the deposit surface or within the deposit pores. This would add to the thickness and density of deposits, respectively.

**Figure D-9 - Wick Boiling In Motion**

Any corrosive contaminant (e.g., acid, caustic, chloride) - will be concentrated many times while in contact with the tube steel. This can result in corrosion and perforation of the tube wall: it is even possible that hydrogen damage can occur, particularly if an acidic contaminant is present. For example, with a concentration factor of 100, 10 ppm of hydroxide in the boiler water will result in 1000 ppm of hydroxide (~12.4 pH) at the tube surface. By analogy, a pH of 5 in the boiler water may correspond to a pH of 3 at the metal surface.

An example of underdeposit corrosion is shown in Figure D-10, on a tube sample which was previously cleaned to remove deposition that covered the roughened area. At one spot, corrosion penetrated nearly 100% of the wall

thickness. The corrodent in this case was identified as caustic (sodium hydroxide), which was present in the boiler water.

**Figure D-10 - Underdeposit Corrosion**

While it may be related to phase separation rather than film boiling, we have seen signs (i.e., white deposit layers at the interface) of steam blanketing in the tops of generating bank downcomer tubes of recovery boilers. Contributing factors vary but may include boiler design, feedwater temperature, and plugging of the fireside of the generation bank tubes which channels more heat to a smaller area of the generation bank. Concentration of salts in these areas also may contribute to waterside corrosion.

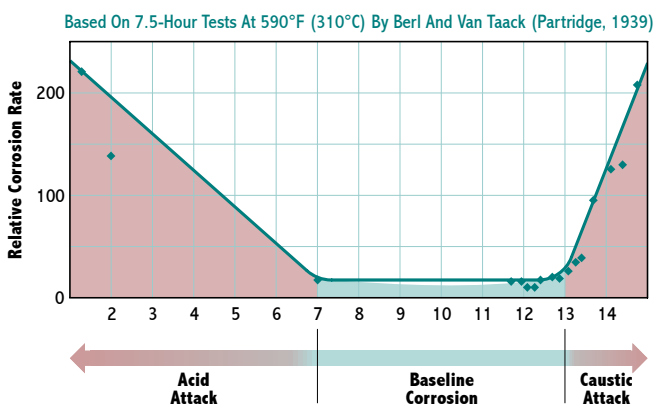
### Effect of Boiler Water pH On Corrosion

There are numerous boilers that have experienced low boiler water pH values from the improper use of monosodium and disodium phosphate or from sulfuric acid entering with the makeup water from the demineralization system. If no chloride contamination is present and the upset is of relatively short duration, often little or no damage results. Also, there have been facilities that have guidelines that allow operation at very acidic pH values (41). However, as indicated in the following discussion, this practice is extremely risky and is inconsistent with TAPPI guidelines (1).

Generally, the most important parameter to monitor and control during normal operation in the steam/water cycle is boiler water pH. The minimum solubility for magnetite (protective iron oxide on steel surfaces in the boiler) at operating temperatures occurs at pH values of about 8.5-11.5 (measured at 25°C) (p. 773 of Reference 16,42). Additionally, steel corrosion (in deaerated water) is minimized in this range. Figure D-11 presents the relative corrosion rate measured on steel by water at 390°C (590°F) (43). The band of minimum corrosion in these short-term (7.5 hours) tests extended to a wider pH range (7-13). At higher and lower pH values, corrosion rates increase dramatically.

Theory and experience dictate that pH values be maintained in the alkaline region (>8) to minimize corrosion. However, pH alone is not the sole indicator of corrosion. Boilers on all-volatile treatment (AVT) with copper alloys in the feedwater system routinely have boiler water pH values of only 8.5-9.0. Low or moderately low pH values due to acid contamination or in the presence of salts (such as sodium chloride) is much more corrosive than just low pH from a lack of alkali. Failure to maintain sufficiently elevated pH values can result in significant boiler tube damage in a matter of hours - depending on the heat flux in the water-wall tubes and the boiler water composition at the time of pH depression.

**Figure D-11 - Effect Of pH On Corrosion Rate Of Steel By Water**



For example, a new 900 psig coal-fired boiler was operated at a boiler water pH of 6.7-7.6, with 5-10 ppm of sodium chloride, evaporated makeup, and no chemical treatment (44). Tube failures were experienced in four days (<100 hours) due to hydrogen damage in waterwall and generation bank tubes, and extensive iron oxide deposition and corrosion was experienced throughout the boiler (44). Other 850-900 psig boilers that have experienced hydrogen damage at moderate pH values include one operated at 8.1-9.0 pH for two years, and two at 8.7-9.6 for 2-7 years (45). While these experiences are mainly from the power industry, they indicate potential corrosion problems from moderately low pH values. Numerous failures from caustic attack also have occurred (45).

**Phosphate Treatment**

For boilers with demineralized makeup, the conventional way to control boiler water pH is through the addition of one of the sodium compounds listed in Figure D-12. Most facilities use trisodium phosphate (TSP) and/or disodium phosphate (DSP) or solutions based on these compounds. While their use is discouraged for normal operation, sodium hydroxide (caustic soda) and monosodium phosphate (MSP) also are sometimes used.

Sodium hydroxide is included as it is used for emergency response to low boiler water pH values. Also, some facilities with high organic levels in the feedwater (which decompose to organic acids) may not achieve sufficient pH elevation with TSP alone. In such facilities, it is suggested to first try feeding crystalline TSP, which contains a little caustic (~0.25 mole of NaOH per mole of TSP) for routine chemistry control. This form of TSP also is easier to dissolve than anhydrous TSP.

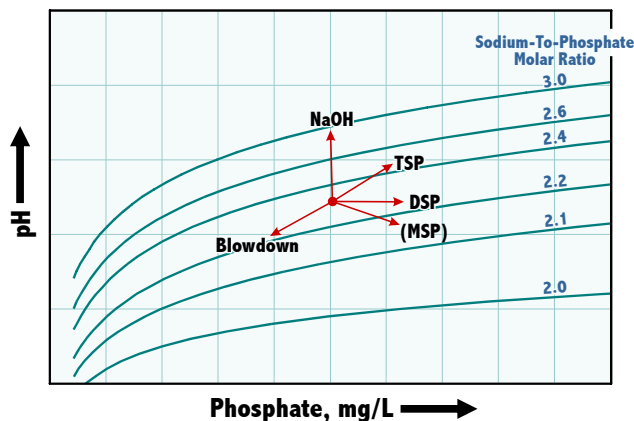
**Figure D-12 - Chemicals For Phosphate Treatment**

Chemical	Actual Na:PO <sub>4</sub> Mole Ratio	pH of 1% Solution	lb PO <sub>4</sub> Per lb Chemical	Na:PO <sub>4</sub> Weight Ratio
Sodium Hydroxide (Caustic Soda)	∞	~13.4	--	--
Trisodium Phosphate TSP - Anhydrous	3.00	12	0.579	0.726
Disodium Phosphate DSP - Anhydrous	2.00	9	0.669	0.484
Monosodium Phosphate MSP - Anhydrous	1.00	5	0.792	0.242

Monosodium phosphate (MSP) is acidic and can contribute to corrosion of the chemical feed line where it enters the boiler. Also, improper use of monosodium phosphate can result in acidic boiler water pH values. At facilities where sodium leakage from the makeup demineralizers and condensate polishers is excessive, monosodium phosphate has been used until the sodium leakage is corrected. However, the use of monosodium phosphate generally is discouraged.

The general effect of each of these compounds on boiler water pH and phosphate is presented Figure D-13.

**Figure D-13 - Molar Ratios And The Effects Of Chemical Addition**

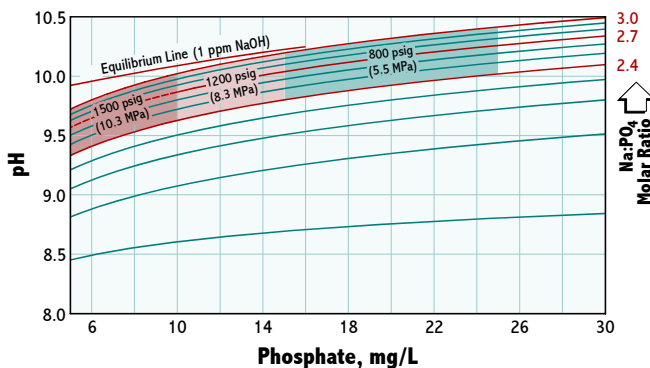


This is a graph of the pH versus the phosphate concentration. Caustic raises the pH and does not affect the phosphate concentration. Disodium phosphate alone tends

to just increase the phosphate without much change in the boiler water pH. However, blowdown decreases everything and will tend to shift levels to the lower left. Therefore, boiler water pH values can be decreased by increasing blowdown and increasing the feed of disodium phosphate. Monosodium phosphate increases phosphate and lowers the pH.

Figure D-14 presents examples of phosphate/pH control curves for 5.5, 8.3, and 10.3 MPa (800, 1200, 1500 psig) recovery boilers. The phosphate concentration range is generally reduced with increasing pressure due to steam purity and phosphate hideout concerns. Phosphate hideout is a reaction between phosphate and magnetite that results in disproportionate loss of phosphate from solution. Classic phosphate hideout is a situation where boiler water pH values rise and phosphate concentrations decrease with increasing load and pH values decrease and phosphate concentrations increase with decreasing load. It generally does not affect boilers operating below 1500 psig, and its prevalence and severity increases with boiler drum pressure.

**Figure D-14 - Typical Examples Of Phosphate/pH Control Curves**



The pH/phosphate control range is bounded by lines for specific sodium-to-phosphate mole ratios. The line with a sodium-to-phosphate mole ratio of 3.0:1 corresponds to trisodium phosphate. Boiler water pH values above the upper line will result in free caustic in the boiler water and in any carryover leaving the steam drum. To avoid free caustic in the steam and in the bulk boiler water, pH values are kept below this line. This is called coordinated phosphate treatment. This type of treatment was first proposed by Whirl and Purcell in 1942 (46) and variations of this basic treatment have been applied since that time. The curves have been refined by Klein, Marcy and Halstead among others (47,48).

For boilers operating at 1200 psig, dryout conditions can produce free caustic if the sodium-to-phosphate mole ratio is over 2.85:1 (49). While dryout of the boiler water should not occur in a properly designed and operated boiler, many have lowered the maximum sodium-to-phosphate ratio for control curves to 2.8:1 or 2.6:1. The lower end of this range

was often chosen as 2.2:1 or 2.3:1 - as below a ratio of 2.15:1 the deposits that form in dryout conditions become increasingly acidic (49). For many boilers, the lower control ranges have been satisfactory and should be satisfactory for boilers up to 8.3 MPa (1200 psig). TIP 0416-03 provides example control curves with lower sodium-to-phosphate mole ratios (i.e., 2.3:1 to 2.6:1) (2). This latter type of treatment is known as *congruent phosphate treatment*.

If the boiler pressure exceeds 1500 psig, higher minimum sodium phosphate ratios may be advised. For example, the minimum suggested sodium-to-phosphate mole ratio to avoid acid phosphate corrosion increases from 2.3:1 at 10.5 MPa (1517 psig) to 2.5:1 at 11.2 MPa (1622 psig) (50). As indicated in Figure D-14, the lower line is sometimes increased to 2.7:1 (dotted line) to avoid operating in the acid phosphate region.

While it commonly affects boilers operating at pressures of 2000 psig or higher, hideout and occasionally acid phosphate corrosion has occurred in a 1500 psig boiler in a refinery (51). In the case cited, phosphate was excessive (20-50 ppm) for this pressure (should have been 5-10 ppm), boiler water pH values fluctuated from 8.7-9.9, sodium-to-phosphate (Na:PO<sub>4</sub>) mole ratios often were below 2.1:1 and corrosion failures were experienced within two months due to acid phosphate corrosion. (51). Such lack of control is rare and should not occur in recovery boilers. Also, small amounts of hideout can be experienced without discernible boiler degradation. Nevertheless, phosphate hideout should be avoided by decreasing phosphate concentrations until hideout is minor or nonexistent. If low-level hideout persists, the amount of hideout can be minimized by allowing the phosphate to decrease and the boiler water pH to rise up to the equilibrium phosphate line, which corresponds to 1 ppm of free caustic (shown in Figure D-14). While not expected to be required for recovery boilers, severe hideout - which prevents the maintenance of a stable phosphate concentration - requires a type of phosphate treatment called equilibrium phosphate treatment (which is not covered herein) (52).

While sodium-to-phosphate mole ratios below 2.4 may be acceptable, use of the higher control range provides more alkalinity and response time in the event of acid contamination of the feedwater. The importance of this should be apparent later in the section on emergency response procedures.

Finally, for those concerned about caustic treatment, the utility industry (which has boilers with much higher heat fluxes) has started to shift from the low congruent ranges to pH values at and above the coordinated phosphate treatment range. In 1994, EPRI recommended controlling the sodium-to-phosphate mole ratios between 2.8:1 and the equilibrium line for both phosphate and equilibrium

phosphate treatment (52). Currently, EPRI recommends a minimum sodium to phosphate mole ratio of 3.0:1.

Potassium phosphate solutions have been applied to boilers to reduce shipping charges (solutions are more concentrated) and to eliminate phosphate hideout. However, as indicated in Figure D-15, the use of potassium phosphate or other potassium compounds should be avoided as corrosion may develop at locations where saturated steam exists.

#### Figure D-15 - Use Sodium Phosphate, Not Potassium Phosphate

- ◆ Potassium Phosphates Are Less Prone To Hideout Than Sodium Phosphates
- ◆ Potassium Salts Are Corrosive At Areas Where Saturated Steam Exists
- ◆ Corrosion Has Been Experienced In Superheaters And Generating Bank Riser Tubes

Corrosion may occur in any location where steam/water phase separation exists. This is most likely to occur in superheaters and in the generation bank. Figure D-16 depicts an example of corrosion in a generating bank tube. Damage was present only on the hot side tube surface; the cold side was not affected. Potassium also was present in a waterwall tube failure in the upper furnace of a recovery boiler that had experienced an excessive accumulation of extremely porous deposits.

#### Figure D-16 - Corrosion By Potassium Salts



In addition to controlling the boiler water pH, phosphates combine with calcium hardness in the feedwater to form less adherent sludges than if phosphate were absent.

### Emergency Response Procedures

In 1992, The Water Treatment Subcommittee of the TAPPI Steam and Power Committee prepared a series of articles

advising response to low boiler water pH, high boiler water pH, silica contamination, black liquor contamination, and feedwater hardness contamination (53,54). TAPPI issued a more formalized guideline (TIP 0416-05), which is a modified version of the earlier guidelines and which now includes suggestions regarding feedwater iron levels (1). The two most important response procedures are discussed herein: Low Boiler Water pH Response and High Boiler Water pH Response.

### Low Boiler Water pH Response Procedures

It has long been known that free acid (pH values below about 4.5) results in rapid corrosion and hydrogen generation from steel - even at room temperature (89). Since pH values can be much lower underneath deposits than in the bulk boiler water, a low boiler water pH can be one of the most catastrophic chemistry upsets.

Figure D-17 (on the following page) presents a condensed summary of the suggested response to low boiler water pH values in Recovery Boilers based on TAPPI guidelines (additional suggestions or information provided by the writer are clearly delineated).

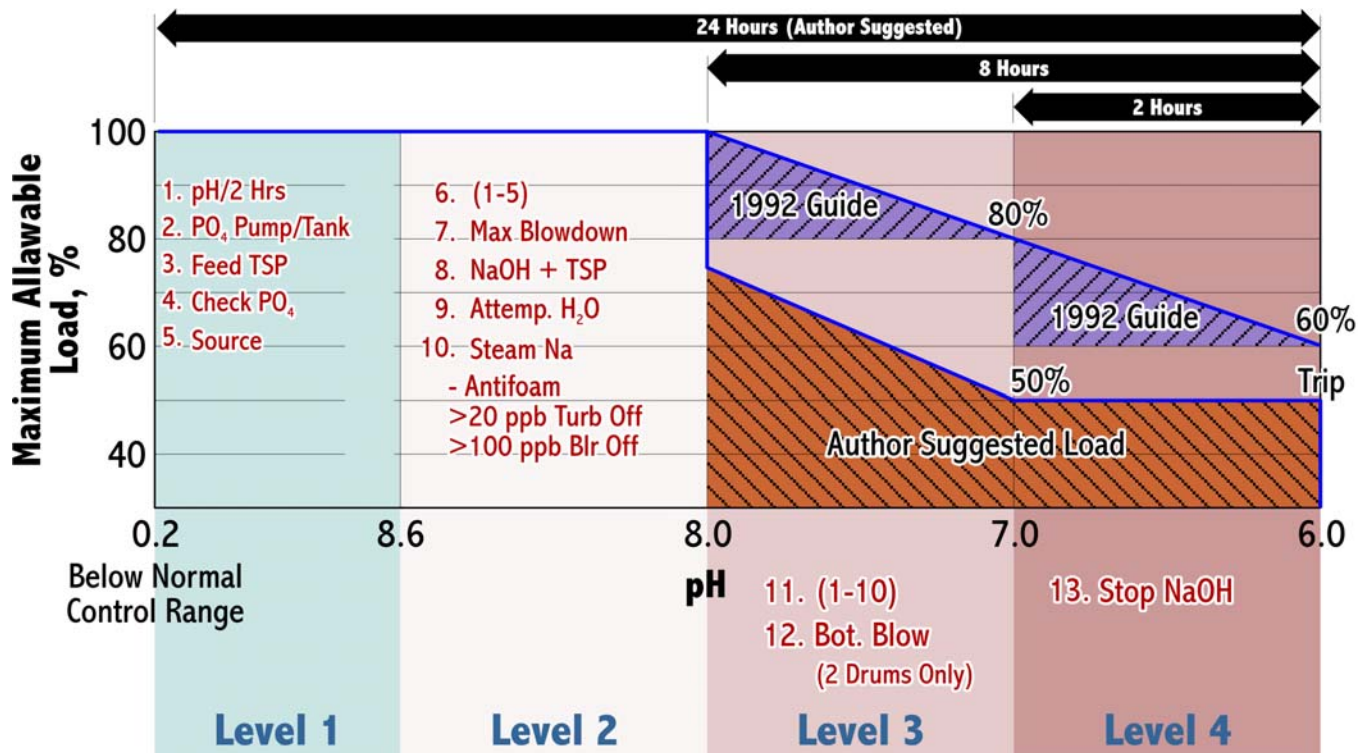
The low boiler water pH response starts at 0.2 pH units below the normal operating range for the boiler. The pH meter calibration should be checked and the pH should be monitored at least every two hours. The feed rate and formulations of the boiler water treatment chemicals applied should be checked. This can involve just checking the pH of the solution. If it is 12.0-12.1, it is probably a 1% solution of TSP. If the pH is lower, dump the tank and prepare a solution of just TSP and demineralized water. In any event, a TSP solution (e.g., 1%) or an equivalent sodium phosphate liquid formulation should be applied to the boiler. The last step involves finding the source. If the formulation is less alkaline than normal, the low pH may just be due to improper chemical feed. Additional sources of low boiler pH are listed in Figure D-18.

#### Figure D-18 - Causes Of Low Boiler Water pH

- ◆ Demineralized Water Contamination
  - Low pH - Regenerant Leak (Acid)
  - Exhaustion Of Anion Unit
  - Hardness Leakage (e.g. Cation Unit)
  - Organics (Pretreatment Upset Or Resin Loss)
- ◆ Condensate Contamination
  - Low pH (Acidic Regenerants For Polishers)
  - Hardness (Raw Water)
  - Organics (e.g. Vapor Contamination Of Evaporator "Clean Condensate" - Only With Some Mill Designs)
- ◆ Sodium Phosphate Feed
  - Wrong Blend (Too Much DSP Or MSP)
  - Bad Or Incorrectly Marked Chemicals

Obviously, if acid is present in the condensate or demineralized water, this will concentrate in the boiler and decrease

Figure D-17 - Low Boiler Water pH Response



the boiler water pH. Low pH values in the demineralized water from sulfuric acid leaking into the effluent during regeneration of a cation or mixed-bed ion exchanger is a common cause for severely low boiler water pH. In North America, the use of sulfuric acid by most facilities is fortunate, because it is much less corrosive to the boiler. Extra caution is required for facilities that use hydrochloric acid. Acid also can be introduced by exhaustion of the anion unit or mixed-bed (although silica levels usually are excessive before measurable acid would be detected). Failures of laterals in makeup or condensate ion exchangers can result in resin loss, decomposition in the boiler, and low boiler water pH.

Hardness in the condensate or in the demineralized effluent also can decrease the pH. When hardness salts deposit in a boiler on coordinated phosphate, they precipitate as phosphates and the resulting solution consists of neutral salts (pH ~7). Once the phosphate is consumed the hardness will react with the trace of hydroxide present and the boiler water pH can drop into the free mineral acid range (e.g., pH 3-5).

Organic matter can decompose in the boiler to form organic acids which suppresses the boiler water pH. In some systems, clean condensate from the evaporators may become contaminated with volatile matter due to steam contamination during evaporator shutdown and cause low boiler water pH values.

Colloidal silica can be introduced with the makeup water. Since colloidal silica can be digested (converted to reactive silica) in a boiler, it can consume some alkalinity in the boiler water and result in much higher boiler water silica levels than expected based on feedwater silica concentrations. Therefore, increasing boiler water silica may correlate with decreasing boiler water pH and alkalinity. This may explain minor changes in pH, but large changes probably would suggest that organic matter or other material entering the cycle at the same time as the colloidal silica may be contributing to the boiler water pH suppression.

If the boiler water pH drops to 8.0-8.6, the first steps are the same as the prior response category (8.6 to 0.2 pH units below the normal boiler water pH). This approach (ensuring prior suggestions were followed first) is followed in all of the TAPPI response guidelines. In this pH range, the blowdown rate should be increased to maximum, and the measured amount of caustic should be mixed in with the TSP to reestablish a normal pH. The phosphate fed to the boiler should be increased to balance the blowdown rate increases.

The remainder of the suggestions at pH 8.0-8.6 are designed to minimize the amount of sodium in the steam to the turbines and superheaters. Compliance requires on-line steam sodium monitoring which unfortunately is not present in many mills. While some facilities monitor the attemperating water conductivity, this parameter often is not sufficiently responsive to ensure satisfactory steam purity. If the attemperating water purity decreases noticeably, consider

discontinuing attemperation, which may require reduction in the boiler load. If the steam sodium increases, TAPPI suggests feeding an antifoam. However, this usually is only considered for lower pressure boilers that receive softened makeup. If the steam sodium exceeds 20 ppb, consider removing the turbine from service to minimize turbine deposition. Each steam system and turbine behaves differently, but steam sodium levels above 10 ppb can result in sticky valves in steam systems and turbine deposits. If the sodium is sodium phosphate from carryover, it will deposit in the first few stages of the turbine. Some sodium salts will deposit just before the condensation region of a condensing turbine and can contribute to corrosion and cracking. Generalized guidelines for industrial turbines manufactured by Westinghouse (now Siemens) recommended immediately shutting down the turbine if sodium in industrial turbines reaches 35 ppb (55). General Electric recommended immediate turbine shutdown above 500 ppb of sodium and specific times at lower sodium levels (56). Consult your turbine manufacturer's recommendations, if available.

Turbine deposits and capacity and efficiency reductions have occurred from carryover and attemperation water contamination from recovery boilers. The capacity reduction will remain until deposits are washed off in a shutdown.

If the sodium exceeds 100 ppb, TAPPI suggests to consider removing the boiler from service to protect the superheater. The critical value will vary with the superheater design, but this seems to be a reasonable limit and cause for concern.

In Figure D-17, the author has added an additional suggested time limit of 24 hours for boiler water pH values below the normal boiler water pH range. Inability to correct the boiler water pH in 24 hours indicates a significant problem or improper response by operators. As a minimum, supervisory personnel should be notified if the source cannot be found or the problem cannot be corrected.

Once the pH drops below 8.0, TAPPI recommends removing the boiler from service if the boiler water pH has been below 8.0 for 8 hours (and some facilities have shorter time limits). The only additional responses recommended were to perform bottom blows of 2-drum boilers every 30 minutes. When the pH decreases below 7.0, TAPPI says "Caution-Discontinue the feed of caustic if the boiler water pH drops below 7.0" (1). At a pH of 6.0 or less it recommends to remove the boiler from service. Before returning the unit to service, eliminating feedwater contamination and considering a boiler chemical cleaning are suggested.

Since caustic addition must cease below a pH of 7.0 (and caustic is in the chemical feed tank), the guide seems to ensure that a boiler will need to be removed from service if the pH drops below 7.0. Since the transition from pH 8.0 to 7.0 can occur very quickly, the author has included

additional suggestions to avoid having the pH drop below 7.0 and thereby avoid removing the boiler from service.

In the 1992 guide for low boiler water pH values, a 20% reduction in load was recommended below a pH of 8.0 and a 40% reduction in load was recommended below a pH of 7.0. It is not clear why this advice was eliminated. Some facilities reduce load below 75% for pH values below 8.0 and below 50% load for pH values below 7.0. Reducing load protects the boiler and helps the operator regain control of boiler water pH for the following reasons:

- A 50% reduction in the load will cut the rate of acidic contamination entering the boiler by half.
- A 50% reduction in load may decrease the rate of deposition (e.g., by a factor of 4). A similar reduction in the underdeposit concentration of dissolved contaminants may be expected.

Incidentally, the 30% minimum load was included in the figure - based on BLRBAC recommendations for minimum load (57).

In addition to the aforementioned guidelines, some plants have suggested a time limit of two hours with more frequent pH monitoring (every 10 minutes or continuous) below pH values of 7.0. These time limits can reduce the amount of corrosion that may be occurring in areas with high concentration factors. Also, the pH can drop rapidly from these pH values and more rapid detection and response is desired.

There are a number of old recovery and power boilers that have experienced short periods of boiler water pH values below a pH of 6.0. Generally, the amount of corrosion was believed to be relatively minor. However, areas that have been partially pitted in the past may experience even greater corrosion and hydrogen damage during subsequent upsets. Also, whether the incident occurred with clean or dirty boiler tubes, before or after a retrofit resulting in a capacity increase on the recovery boiler, with low load during a mill startup or full load, or with or without chloride present, all will affect whether a low pH incident will cause boiler tube damage. If you choose to follow alternative guidelines, the last question you should answer is "Do you feel lucky?"

### High Boiler Water pH Response Procedures

Figure D-19 summarizes the response procedures to high boiler water pH levels in the boiler water from Table 1 of TIP 0416-05 (1). Many of the responses are the same as listed in the low boiler water pH response procedures - except that less alkaline chemicals are applied to the boiler. The TAPPI guide suggests that if the boiler water pH is above 11.0 for 24 hours, that the boiler be removed from service. However, no maximum boiler water pH is listed for immediate trip.

As indicated earlier, detectable corrosion can occur in a matter of hours when the pH is about 13 or higher. Concentration mechanisms on tube surfaces may achieve these values at much lower pH values in the boiler water. A maximum pH for immediate removal from service of 11.5 to 13 is suggested herein, depending on the boiler pressure and degree of concentration at tube surfaces. Also, load reductions may need to be considered at elevated pH values (e.g., 11.5) to reduce concentration mechanisms at tube surfaces, to reduce the rate of ingress of contaminants into the boiler, and to avoid carryover. Also, if the high pH is mainly due to black liquor, then lowering the pH or caustic alkalinity may actually promote deposition of organic matter. Therefore, maximizing blowdown to reduce color within suggested limits is recommended herein.

**Figure D-19 - High Boiler Water pH Response (Based On Table 1 - TIP 0416-05, TAPPI)**

From 0.2 Above Normal pH Range To 10.5	From 10.5 To 11.0	Greater Than 11.0
<ol style="list-style-type: none"> <li>1. pH/2 Hours</li> <li>2. PO, Pump/Tank</li> <li>3. Find Source</li> <li>4. Attemperation Water</li> <li>5. Steam Sodium               <ul style="list-style-type: none"> <li>• Increase Blowdown</li> <li>• Add Antifoam</li> <li>• &gt;20 ppb Turbine Off</li> <li>• &gt;100 ppb Boiler Off</li> </ul> </li> </ol>	<ol style="list-style-type: none"> <li>6. (1-5)</li> <li>7. No NaOH Feed</li> <li>8. Maximum Blowdown</li> <li>9. Bottom Blowdown (Two Drums Only)</li> <li>10. Increase DSP And Possibly Dispersant Feed (To Match Blowdown)</li> </ol>	<ol style="list-style-type: none"> <li>11. (1-10)</li> <li>12. &gt;24 Hours, Remove Boiler From Service</li> <li>13. Find Source And Fix Before Boiler Restart</li> </ol>

#### Author Suggestions

- >11.5 Reduce Load
- >11.5 To 13 Commence Orderly Shutdown, Drain And Flush Boiler

Figure D-20 summarizes the common causes of high boiler water pH values. Large and sudden high pH incidents can result from sodium hydroxide regenerant leaks from ion exchangers in the makeup or condensate system or from black liquor contamination. A cation exhaustion will be sudden, but it usually is detected before significant contamination enters the makeup. Organic fouling of the anion resin can occur suddenly due to poor pretreatment or can gradually worsen. Organic fouling is usually apparent by high sodium hydroxide leakage following a regeneration. This can be indicated by high sodium, conductivity, and pH values following a regeneration and longer rinse times for the anion unit. Cation resin or resin fines in the following anion is less common, but can mirror organic fouling. Following a regeneration of a sodium cycle condensate polisher (i.e., cation resin regenerated with sodium chloride), amine displacement of sodium from the condensate polisher will often result in high boiler water pH values. This effect tends to lessen over time. However, a dramatic overfeed of amine to the feedwater also can carryover with the steam and then cause a large transport of sodium off of the condensate polishers.

#### Figure D-20 - Causes Of High Boiler Water pH

- Makeup System
  - Regenerant Leak (Caustic)
  - Cation Exhaustion
  - Organic Fouling Of Anion
  - Cation Resin In Anion
- Condensate
  - Black Liquor Contamination
  - Sodium Cycle Polishers - Excessive Amine Displacing Sodium
  - Mixed Beds - Regenerant Leak (Caustic)
- Boiler Treatment Chemicals - Misfeed

#### Phosphate/Caustic Treatment

Phosphate/Caustic treatment, or the maintenance of phosphate and free hydroxide in boiler water, continues to be used in industrial boilers with softened feedwater that operate at pressures up to 900 psig - as the sludges formed are more fluid. Boilers operating at 1200 psig and higher are much more susceptible to caustic attack (about 11 boilers operating at 1200-1500 psig had this attack) (71). The advantages and disadvantages of this treatment are summarized in Figure D-21.

#### Figure D-21 - Boiler Water - Caustic/Phosphate

- Advantages
  - Less Adherent Deposits With Calcium
  - Corrosion Protection For Steel (High pH)
- Disadvantages
  - Caustic Corrosion Beneath Deposits, In DNB Or Steam Blanketed Areas
  - Greater Tendency To Carry Over
  - Experience Indicates Higher Caustic Corrosion Potential With Demineralized Makeup Than Softened Makeup

The most common type of caustic attack of waterwall tubes was commonly referred to as caustic gouging because the corrosion would form a deep gouge in the tube surface and it was thought to be exclusively caused by caustic. However, it has since been found that there are a number of corrodents that can result in similar attack.

#### Chelant Programs

Chelant programs were promoted in the 1960's, but their use generally fell into disfavor due to rapid corrosion that resulted from improper application or upset conditions. There are industrial facilities that use chelants, and the use of chelants has been recently promoted as a means of avoiding chemical cleanings for 600-1200 psig boilers on naval ships (72). However, the greater risk of corrosion with chelant treatment requires greater attention than for phosphate treatment in recovery boilers.

The advantages and disadvantages of Chelant Programs are presented in Figure D-22. The organic chelants used for boiler water treatment have been limited to ethylenediaminetetraacetate (EDTA) and nitrilotriacetate (NTA). The

purpose of these materials is to form soluble complexes with hardness and with ferrous ions so these materials may be removed from the boiler with the continuous blowdown. It has been noted that excess chelant will attack clean boiler surfaces, particularly if oxygen is present, therefore, it is most important that good deaeration be practiced (73).

#### Figure D-22 - Boiler Water - Chelant

##### Advantages

- Hardness And Iron Oxide In Solution
- Less Frequent Chemical Cleanings

##### Disadvantages

- Can Corrode Boiler Steel If Not Properly Controlled
- Must Control Dissolved Oxygen
- Difficult To Control Residual

Investigations have been made to determine the effect of competing anions (phosphate for calcium, and silica for magnesium) in the chelation process (74,75). The results showed that precipitates did form in the presence of a free excess of EDTA or NTA or a combination of the two to the extent that the precipitation of calcium by phosphate defeated the purpose of adding the chelant. Test results illustrated the need for adequate pretreatment of the water by demineralization to reduce hardness. It was stated by the authors of one paper that addition of chelant is no substitute for good pretreatment (74). It also was noted that when chelant residual was increased in an effort to counteract this precipitation, the iron residual in the blowdown increased, indicating greater corrosion of boiler metal (75). This same paper noted that addition of a polymer to the chelant treatment resulted in better transport of metals to the blowdown.

Other investigators studied deposition in a 4.1 MPa (600 psig) boiler which was on a chelant treatment program (76). Again, evidence of precipitation of calcium phosphate and magnesium silicate was found. The program in use was a combination of EDTA and NTA. When phosphate was entirely removed from the boiler water, deposition was found to consist of layers of calcium and magnesium silicates.

The papers cited show that even advocates of the use of chelants recognize that there are shortcomings in their use in boiler water treatment. This is not to detract from the cases where chelants have been successfully used to prevent buildup without causing corrosive damage. This information emphasizes the necessity of a thorough evaluation before using these rather aggressive materials and the need for very careful control of boiler water chemistry while chelants are in use.

### Polymer Dispersant Programs

Polymers are currently incorporated into phosphate solutions used at many pulp and paper mills. However, since vendors often oversee the treatment program and active polymer levels are usually not monitored, operators

and other mill personnel are sometimes not aware of their inclusion in the formulation. Advantages and disadvantages of polymer dispersant programs are presented in Figure D-23. Several chemical manufacturers and vendors have proposed using boiler water treatment consisting of polymers only. These programs, which may use one polymer or a mixture of polymers, are intended to leave boilers as clean as is possible with a chelate program, but with no more corrosion damage than associated with phosphate treatments (77). Tests have been made to compare results of single polymers (or polymer mixtures) with EDTA by alternating treatment to the boiler. In one test program, iron transport by EDTA was reported to be much higher than with the polymer; this was attributed to high corrosion rates (77). The polymer appeared to transport all of the iron introduced into the boiler with feedwater without adding corrosion products. The author claimed that this polymer program produced boiler cleanliness unobtainable by any other program in use for boiler water treatment.

Godfrey reported that excessive feed of polymers can increase corrosion of steel surfaces: "In short, polymer and chelant molecules possess no intelligence that allows them to differentiate between the magnetite in a deposit and the magnetite that comprises the passive film in areas with no deposit" (84). A polymer feed rate over 5 ppm to the feedwater resulted in increased corrosion of a paper mill boiler - based on ferrous iron monitoring of the boiler water (84). Only about 3 ppm of dispersant was needed for iron dispersion at this facility. The nature of the corrosion was not reported. It was indicated that polymethacrylate has about 30-60% of the corrosivity of polyacrylate. For example a dose of 15 ppm of polymer resulted in 22 ppb of ferrous iron in the feedwater with polymethacrylate and 37 ppb of iron in the feedwater with polyacrylate (84). However, these corrosion rates are a fraction of that expected with chelant treatment.

#### Figure D-23 - Boiler Water - Polymer Dispersant

##### Advantages

- Better Transport Of Iron Oxide
- Less Deposition Of Hardness

##### Disadvantages

- Difficult To Control Residual
- More Blowdown Needed
- Inhibits Natural Settling In Drums

Another paper reported on a polymer which transports iron oxide (or inhibits deposit growth) more effectively than the polymers previously used for this purpose (78). Trials with boiler pressures up to 10.3 MPa (1500 psig) were successful. There was no evidence of on-line cleaning or transport of old, hard magnetite deposits, although there may be some effect on loosely adherent iron oxide. A few mills on this polyphosphonate program were surveyed in 1998, and at least one mill reported a reduction in iron



oxide deposits in the areas sampled. Similar results have been reported for boilers on other dispersant programs.

Reports of deposit removal from areas normally sampled may indicate a pending problem. Reports from some mills employing dispersant treatments indicate that deposits removed from low heat transfer rate areas (which can be inspected) had precipitated in high heat transfer areas of the waterwalls. In some cases, the precipitates led to tube failures. Also, unusually heavy deposits occasionally have been found in upper furnace tubes in boilers that use polymers. The upper furnace usually is not considered an area of high heat flux, but the proportion of steam increases as the steam/water mixture flows up the tube and there may be a transition reached where suspended or dispersed matter will deposit. In programs without dispersants, deposits will form everywhere including colder areas and there will be less to form localized deposits in areas with higher heat flux, reduced circulation, and/or high steam qualities.

It would be prudent to chemically clean any boiler with heavy deposits, or one formerly on phosphate treatment, before changing to dispersant or chelant treatment. In-service cleaning has an intriguing sound, but this may turn out to be merely relocation of deposition - to an area where tube failures can result.

### Degradation of Polymer Dispersants

Polymers degrade due to high temperatures, elevated dissolved oxygen levels, and for polycarboxylic acids, low pH conditions. Since polycarboxylic acids such as polyacrylate or polymethacrylate have been some of the most widely used polymers for boiler water treatment, a greater amount of information on their degradation also was available.

Thermal decomposition (by decarboxylation) of polyacrylate (to carbon dioxide and a partially carboxylated hydrocarbon, which was water insoluble at low temperatures) was rapid at temperatures above 530-660°F (288-349°C) (83). However, it is cautioned that there clearly were some significant typographical errors (seconds for minutes, etc.) in this reference. The percent iron dispersion was indicated to be reduced by twice the decarboxylation rate. (Therefore 100% of iron dispersancy performance is lost at 50% loss of carboxylate.)

Masler found no significant change in calcium carbonate dispersion as a result of 9.5% and 16.1% loss of carboxylic acid functionality for polyacrylate and polymethacrylate, respectively (86). This level of decomposition resulted from exposure to only 250°C (482°F) for 18 hours at a pH of 10.5(86). Perhaps the lack of change in calcium dispersion was due to a threshold inhibition effect rather than a stoichiometric complexation effect. Masler's study also

suggested that polymethacrylate was more subject to thermal decomposition (86).

Decomposition (decarboxylation) of polyacrylate increases rapidly below a pH of 8 (83). This effect is believed to be due to the liberation of carbon dioxide with acid addition which would favor the decomposition reaction. However, the exact mechanisms are believed to be more complex and involve intermediate species (85). About 50% loss of carboxylate may be experienced in a fraction of a day at a pH of 6.5 and is essentially instantaneous at a pH of 4.5 (85). Increased decomposition at low pH is expected for other carboxylic acids (e.g., polymethacrylate). During a low pH upset, the boiler water will be much more concentrated underneath of the deposits. Therefore, during a low boiler water pH upset, the pH may be significantly lower (more acidic) on tube surfaces in areas of high heat flux, and polymer decomposition rate would be accelerated on tube surfaces.

As indicated by Godfrey, after 15% decarboxylation from solutions at a pH of 4.5, a "solid waxy residue was recovered. This residue was soluble in alcoholic KOH. Because of the dissociation of polyacid at a pH of 10 about 25% decarboxylation could occur before any significant precipitation was observed" (85). This suggests that the thermal decomposition of dispersants based on polycarboxylic acids could be a small source of organic deposits (if the tube temperatures underneath deposits are much higher than saturation). However, with the possible exception of the Spencer study, we have not located laboratory data evaluating this potential for the specific dispersant blends used in boilers. Since there are very few studies of the decomposition of polymer solutions, the contribution of degraded dispersant polymers to past and future boiler deposits is still somewhat of a speculation.

Surprisingly, the decomposition rate of polyacrylate did not increase with increased heat flux in the laboratory (83).

However, this probably is not representative of an operating boiler tube where tube metal temperatures beneath deposits may rise significantly due to the combined effect of waterside deposit accumulations and heat flux - especially if a low pH upset is experienced (combined effect of low pH and high temperature).

### Combination Programs

Several reports of treatments using polymer/chelant mixtures with and without phosphate are available (79,80). One paper says that very good transport of hardness and iron oxide through the boiler was obtained with phosphate plus a polymer, while EDTA plus a polymer gave results superior to EDTA alone. The final conclusion reached by these investigators was that the mixture of EDTA plus polymer gave the best results - as far as boiler cleanliness was concerned - of all programs evaluated (79). However,

the authors cautioned that corrosion should be controlled at its source (the feedwater system), corrosion products should be removed with polishers, and heavily contaminated streams should be diverted to waste rather than depending on internal boiler water treatment to do the whole job.

A second report on tests of combined treatment agents also found that EDTA plus a polymer produced the best results for transporting iron oxide to the blowdown (80). Phosphate was used as a pH buffer with very low hardness water. These authors advise good deaeration of water, including use of chemical oxygen scavengers, when employing chelants as part of the boiler water program. Chelants combined with dissolved oxygen can be particularly corrosive to economizers, but all recovery boiler water treatment programs require good control of dissolved oxygen in the feedwater - primarily to protect the economizer and copper components in the steam system. Polymers and chelants also can experience significant (50-95%) degradation in the event of high feedwater dissolved oxygen levels (81).

### Boiler Water Treatment Summary

The different approaches discussed in this section constitute a wide choice of boiler water treatment for specific objectives. All have been successful in some instances, with proper pretreatment of makeup and feedwater and careful control of boiler water chemistry. There are possible problems and/or dangers associated with each method, as well as the possible rewards expected from usage. No boiler water treatment program should ignore the essentials of first preparing a suitable makeup water for the cycle, reducing preboiler system corrosion to the extent possible with chemical and mechanical treatment, and then removing as much of the corrosion products remaining (or any other contaminants) with condensate polishing or diversion of the contaminated streams to waste. This is the basis of a successful boiler water treatment program.

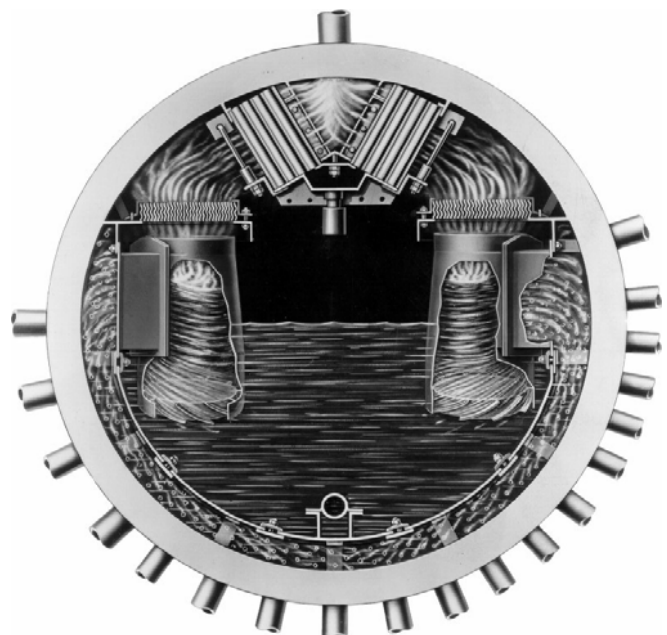
### APPENDIX E: STEAM PURITY CONSIDERATIONS

Figure E-1 presents a diagram of flow in a steam drum during operation. The steam/water mixture enters the steam drum from riser tubes and pipes and is diverted to the cyclone cans. The mixture enters the cans on a tangent which results in a cyclone in the cans with water flowing down and steam flowing up. The partially dried steam flows through a series of metal plates (sometimes called chevrons) which remove additional droplets, and then through the final separators. The overhead separators are sometimes called dryers. The steam leaving is relatively free of droplets of boiler water. Boiler water that leaves with the steam is called carryover.

While carryover is low in modern recovery boilers, a trace of boiler water is present and dissolved solids in the boiler water will sometimes determine the steam purity. This is

particularly true if the boiler water is concentrated to the point at which it starts to foam. To minimize dissolved solids in the steam and boiler water, the blowdown (boiler water flow to blowdown tank) is usually left open at a set flow rate to fix the cycles of concentration (number of times the feedwater is concentrated in the boiler water). Boiler water conductivity (general measure of dissolved solids) and silica (discussed later) usually are the primary chemistry factors that influence the blowdown rate setting. If makeup and condensate purity are very good, blowdown can be set at 1% or less of the feedwater flow. This results in 100 cycles of concentration of feedwater contaminants in the boiler. If the boiler happens to use dispersants, the blowdown rate also should be set at a level that purges most of the dispersants before they decompose.

Figure E-1 - Typical Cyclone Separator In Steam Drum



Courtesy Of Babcock & Wilcox

Steam leaving the steam drum is routed to the superheater. After a primary superheater section, desuperheating (also called attemperation) water is added and then the steam passes through a secondary superheater to the main steam header. Attemperation rates in recovery boilers can be over 7% of the total steam flow. The desuperheating water supply can be from a sweet water condenser (saturated steam condensed in a shell and tube heat exchanger) or from the feedwater line. Sweet water condensers are standard for new recovery boilers and are recommended for consideration for all boilers as retrofits.

The two main sources of steam purity upsets are boiler water carryover and contaminated attemperation water. The most common feedwater contaminants that noticeably reduce steam purity usually are as follows.

- Sodium compounds
- Silica

The sodium compounds can deposit throughout the turbine depending on the type and amount. Silica usually deposits in the last stage. Experience indicates that low levels of silica deposition from slightly elevated levels can be experienced without significantly affecting turbine operation whereas sodium deposits often cause noticeable reductions in load fairly quickly. Varying amounts of these contaminants are introduced with the feedwater during normal operation. During upset conditions where black liquor, oil, or raw water enter the boiler with the feedwater, organic matter can enter the boiler and carbonize on tube surfaces. These materials also can contribute to boiler water foaming and carryover of boiler water salts into the steam. A summary of various sources of carryover is presented in Figure E-2.

#### Figure E-2 - Turbine Deposition Sources - Carryover From Boiler

- ◆ High Drum Level
- ◆ Improper Operation Of Steam Separation Equipment (Mechanical Failure)
- ◆ Boiler Water Contamination
  - High Conductivity
  - High Alkalinity
  - High Suspended Solids
  - Organics
- ◆ Excessive Steam Flow
- ◆ Erratic Steam Flow

Figure E-3 presents the common contributors to attemperation water contamination for facilities with feedwater attemperation. For facilities with a sweet water condenser, causes may include a tube leak or carryover (the steam supply may bypass some of the steam separation equipment).

#### Figure E-3 - Turbine Deposition Sources - Contaminated Attemperation Water

- ◆ Demineralized Makeup Leakage/Upset
- ◆ Condensate Contamination
- ◆ Condensate Polisher Leakage/Upset
- ◆ Leak In Blowdown Heat Exchanger
- ◆ Seal Water Inleakage On Pumps

In addition to mechanical carryover of boiler water, silica is volatile and soluble in steam - depending on the boiler pressure. Therefore, a certain amount of silica will transfer from the boiler water to the steam in the absence of carryover. If the silica exceeds 20 ppb, it will tend to deposit on the last stage of condensing turbines. To avoid this deposition, silica in the boiler water usually is monitored and the concentration is controlled based on the boiler pressure (see Figure F-2 in Appendix F).

## APPENDIX F: ADDITIONAL CHEMISTRY TESTING

The body of the presentation introduced only five chemistry tests used for the monitoring and control of steam/water cycle chemistry. However, there are a half dozen other tests which the recovery boiler operator will need to ensure proper control. This additional chemistry testing is discussed in this Appendix.

### Alkalinity

Alkalinity is a measure of the neutralization capacity of the boiler water. It literally is the amount of acid the boiler water can absorb before reaching certain low pH values. The tests normally involve titrating with acid to obtain a color change of a colorimetric indicator. Most mills have two indicators: P-alkalinity indicator and M-alkalinity (or Total alkalinity) indicator. The P-alkalinity always is phenolphthalein, which changes from pink to clear at a pH value of about 8.2-8.3. There are a number of commonly used M-alkalinity indicators: methyl orange, methyl purple, bromcresol green-methyl red, and others. These titrate to pH values of 4.5-5.2. Because of the nature of the ions usually present, the pH changes rapidly in this pH range. Therefore, the M-alkalinity indicators yield fairly comparable results.

The primary purpose of P-alkalinity and M-alkalinity testing is as a backup monitoring for the boiler water pH - as onsite pH readings can be grossly in error due to problems with sample temperature control and fouled or broken probes.

While P-alkalinity and M-alkalinity were originally developed to model solutions of hydroxide, carbonate, and bicarbonate, they also have been found to be very useful for modeling phosphate solutions as well. Relations are available for indicating the free caustic or sodium to phosphate mole ratio for phosphate solutions from phosphate, P-alkalinity, and M-alkalinity.

The free hydroxide alkalinity can be estimated from the P-alkalinity and M-alkalinity (i.e., 2P-M). The hydroxide alkalinity normally is low in boilers with demineralized makeup. Industrial boilers with softened makeup often determine the hydroxide alkalinity directly by reacting the sample with barium chloride and then titrating to the P-alkalinity endpoint. These boilers usually often maintain caustic alkalinity at three times the silica concentration to avoid the formation of hard, insulating silicate deposits.

### Silica

A summary of the key information to understand about silica is summarized in Figure F-1. Silica is not corrosive and elevated silica will result in the gradual deposition on the tail end of condensing turbines. While this can reduce

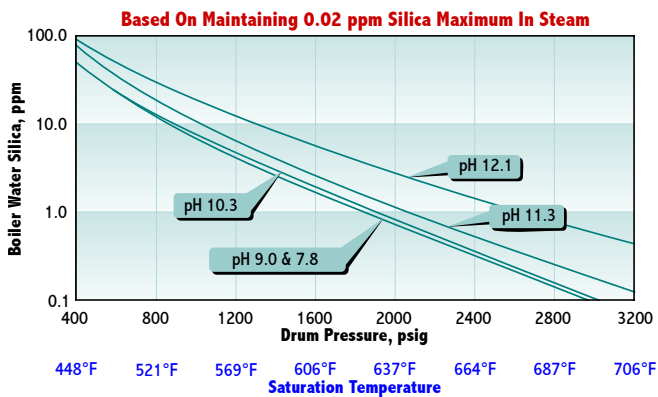
turbine efficiency, it is not usually sufficiently severe to warrant removal of the boiler from service.

### Figure F-1 - Silica (SiO<sub>2</sub>)

- ◆ A Soluble Form of Sand That is Semi-volatile in Boiler Water and Deposits on the LP End of Condensing Turbines
- ◆ Units:
  - ppb SiO<sub>2</sub> = µg/L SiO<sub>2</sub>
  - 1 ppm = 1 mg/L = 1000 ppb
- ◆ Expected Values
  - Demineralized Water/Steam: <20 ppb
  - Condensate/Feedwater: <20-50 ppb
  - Boiler Water: See Curve
- ◆ Control
  - Boiler Blowdown Based on Silica Curve
  - Good Makeup Treatment
  - Sewer Condensate

Silica usually is controlled in the boiler water to avoid steam silica levels less than 20 ppb. This is achieved by keeping the boiler water silica less than the lower line in Figure F-2. For boilers (e.g., <800 psig) which may operate with boiler water silica levels over 10 ppm, hydroxide alkalinity should be present in sufficient amounts to inhibit the formation of extremely insulating silica scales in the boiler.

### Figure F-2 - Maximum Boiler Water Silica Concentration vs Drum Pressure At Selected Boiler Water pH



## Iron

Figure F-3 presents a summary of iron testing, and the normal mode of control. The main control of iron transport to the boiler is through the control of amine feed in the condensate and feedwater and the dissolved oxygen levels in the feedwater. Ideally, the pH would be much higher to minimize iron transport (e.g., 9.5-10), but this would result in excessive copper transport. Increasing the condensate/feedwater pH to 9.2 to 9.4 has been used to minimize iron transport in mixed metallurgy systems in pulp and paper mills, where copper transport has not been a problem (i.e., small proportion of copper surfaces in the cycle).

Excessive condensate dissolved oxygen levels also may contribute to increased iron transport, but the recovery boiler operator often does not have control over the offending condensate system.

### Figure F-3 - Iron

- ◆ Corrosion Product Formed from Steel and Iron Corrosion
- ◆ Mainly Present As Suspended Matter in Condensate and Feedwater. Oxide (Fe<sub>3</sub>O<sub>4</sub>) Determined by Filtration (0.45 µm) and Color Formed on Filter Pad.
- ◆ Total Iron (Fe) Is Determined by Colorimetric Test on Spectrophotometer.
- ◆ Units:
  - 1 ppb Fe = 1 µg/L Fe
  - 1 ppm Fe = 1000 ppb = 1 mg/L
- ◆ Main Control
  - Condensate Polishers and/or Magnetic Filters
  - Amine Feed: Condensate/Feedwater pH (8.8-9.4) & Conductivity (2-6 µS/cm). pH Ideally 9.5-10 for Minimum Iron Corrosion (Boiler).
  - Dissolved Oxygen of 2-10 ppb in Feedwater

## Copper

As indicate in Figure F-4, copper can be present in the condensate due to corrosion and erosion of copper alloys in the steam/condensate system. Copper and copper alloys can be present in dryers, steam heating coils, feedwater heaters, and sweet water condensers. The main means of control is minimizing dissolved oxygen (the latest studies indicate 2 ppb or less). The optimal pH range for minimizing copper pickup traditionally was found to be 8.8-9.0 in old mills, but satisfactory copper levels have been noted in some systems with higher pH values (up to 9.2-9.4).

### Figure F-4 - Total Copper

- ◆ Corrosion Product Formed from Copper Corrosion/Erosion
- ◆ Can Be Present In Suspended or Dissolved Form in Condensate and Feedwater
- ◆ Total Copper (Cu) Is Determined by Colorimetric Test on Spectrophotometer
- ◆ Units:
  - 1 ppb Cu = 1 µg/L Cu
  - 1 ppm Cu = 1000 ppb = 1 mg/L
- ◆ Main Control
  - Dissolved Oxygen of <2 ppb and Oxygen Scavenger Residual
  - Amine Feed: Condensate/Feedwater pH (8.8-9.4) & Conductivity (2-6 µS/cm). Minimum Corrosion at pH <9.0-9.3.
  - Condensate Polishers

However, the higher conductivities from the higher amine levels can obscure detection of contamination, which results in increased copper corrosion. Also, increasing the pH above 9.0 can increase copper transport if dissolved oxygen levels are elevated in the steam/condensate system. The condensate/feedwater pH and conductivity limits must be tailored for each facility to minimize iron and copper

transport. Condensate polishers can be effective at removing copper and copper oxides. However, more elaborate regeneration and backwashing procedures sometimes are required to avoid the buildup of copper in the bed.

Figure F-5 presents a summary of the ASME limits for iron and copper in feedwater for industrial boilers (87). The total corrosion products column is not listed by the ASME, but it shows the steady decline in corrosion product limits with increasing boiler pressure.

**Figure F-5 - Feedwater Corrosion Product Limits**

Boiler Pressure, psig (Mpa)	Iron, ppb	Copper, ppb	Total Corrosion Products, ppb
451-600 (3.11-4.14)	<30	<20	<50
601-750 (4.15-5.17)	<25	<20	<45
751-900 (5.18-6.21)	<20	<15	<35
901-1000 (6.22-6.89)	<20	<10	<30
1001-1500 (6.90-10.34)	<10	<10	<20

### Organic Matter - Color/Turbidity Readings

Harmful organic matter is the hardest thing to measure in an all steel cycle. Organic matter, particularly colloidal organic matter, can harden on tube surfaces and form extremely adherent deposits which can lead to high tube temperatures and underdeposit corrosion.

Total organic carbon analyses are of limited value because the amines applied for condensate/feedwater pH are organic compounds. This leaves qualitative tests such as color and turbidity - which can be affected by other substances. This complicates the setting of definitive chemistry limits for the industry. Figure F-6 presents a summary of some of the tests available and suggested limits.

A number of mills have found boiler water to be 5-12 color units (or less) and have used boiler water alarm (action) and maximum limits of 20 and 50 color units (Co/Pt), respectively.

**Figure F-6 - Organic Matter (Color or Turbidity)**

- ◆ Colloidal Organic Matter Can Form Adherent Deposits On Tube Surfaces. Turbidity and Color Can Indicate Contamination.
- ◆ Color
  - Units: Pt/Co Units, Calibrated With Platinum Cobalt Standard
  - Light Absorbed at Wavelength of 455 nm on a Spectrophotometer
- ◆ Turbidity
  - Units: Nephelometric Turbidity Unit (NTU) on a Turbidimeter. Measure of Light Diffracted to 90° Angle. This Is the True Turbidity Measure.
  - Units: Formazin Turbidity Unit (FTU) Measures Absorbance at a Wavelength of 450 nm on a Spectrophotometer. If No Color Is Present, 1FTU=1NTU.

### ◆ Expected Values

- Condensate: <1 NTU
- Boiler Water Color: <5-12 Pt/Co (>20 Pt/Co is Alarm, 50 Pt/Co is Max. Limit)
- Suspended Iron Can Read As Turbidity (About 20 ppb Fe / NTU) or Color

### ◆ Sources: Black Liquor, Raw/Mill Water, Makeup Plant Leakage

## Sodium

Sodium monitoring in steam is about the only reliable means for ensuring satisfactory steam purity for most boilers. Specific conductivity and pH only provide an indication of carryover in gross carryover incidents. Silica is volatile, so it is more complicated to determine if carryover may actually be occurring using steam and boiler water silica levels. As indicated in Figure F-7, sodium levels usually are and should be normally <5 ppb. Turbine manufacturers usually set limits at 10 ppb or 20 ppb depending on the turbine.

**Figure F-7 - Sodium In Steam**

- ◆ Sodium (Na) Is a Direct Indication of the Nonvolatile Solids in the Steam.
- ◆ Units: ppb Na = 1 µg/L = 0.001 ppm = 0.001 mg/L
- ◆ Normal Levels <5 ppb in steam
- ◆ Alarm Levels
  - >10-20 ppb Deposits on Condensing Turbines and The Turbine Manufacturer's Warranty Limit is Usually 10 ppb or 20 ppb.
  - >10 ppb Causes Sticky Valves in Some Steam Systems
- ◆ Control
  - Boiler Water Carryover: Blowdown, Drum Level, Stable Steam Flow, and Maintain Steam Separators
  - Feedwater Attemperation Water: Control Condensate and Makeup Purity

## Particle Counters And Monitors

Indications of particulate matter also can be provided by particle monitors (PM) and particle counters (PC). Particle monitors measure the fluctuation in light intensity and provide a particle index (PI) value. There are two types of particle counters - those which rely on light blocking and those which rely on light scattering. Light blocking (PC) counts the number of times shadows are cast by particles 1-2 µm to 100 µm. Light scattering (PC) determines the number of particles (down to 0.05-2.0 µm - depending on the instrument) based on the amount of light scattered. In addition to a total particle count, PC units usually can provide a breakdown of the number of particles in several particle size ranges - although total counts are often the most useful. PC units have been used for years to evaluate filter performance in the semiconductor and municipal water treatment industries. In 1995, the American Water Works Association (AWWA) published "A Practical Guide To Online Particle Counting" (95). While this is an excellent document, it is cautioned that there were a number of

PC and PM units which were either unavailable or not considered at the time the document was prepared. PM units were used in the early 1990's to indicate major contamination incidents of various types of suspended matter (e.g., hardness precipitates and iron oxides) in paper mill condensate and makeup water (91). Both PM and PC units have been used more recently to monitor corrosion product transport in power plant condensate, feedwater and steam (92). Laboratory studies found that the particle counts and concentration correlations for magnetite (~700 counts/mL for 25 ppb), hematite (~108 counts for 25 ppb), and copper (~42 counts for 25 ppb) were much different (92).

Also, a consistent correlation between particle counts and corrosion products was not found for the on-line evaluations (92). Part of this lack of correlation was attributed to the normally low iron concentrations (average less than 0.5 ppb) and high proportion of metals below 2  $\mu\text{m}$  in diameter (92). However, the analyzers did find some rather large upsets in iron concentrations that were primarily attributed to operational changes - although a slight change in dissolved oxygen may have contributed to one upset (92). Greater use of PC and PM units is expected in the future.

### **Oxidation Reduction Potential (ORP)**

The oxidation reduction potential (ORP) has been used for years to control chlorination and dechlorination systems in makeup and wastewater treatment applications. It is also a commonly recommended monitor for balancing copper and iron corrosion product transport in high pressure power plant cycles. ORP provides a relative measure of oxidizing (e.g., oxygen) and reducing (e.g., hydrazine) species in water. For mixed metallurgy power plant cycles, the control range usually is within the range of -120 mV to -350 mV (at 25°C) as measured by a platinum electrode and saturated silver chloride reference electrode. The exact control range should be tailored to a particular plant and be based on corrosion product transport data. Plants with a very large proportion of copper or copper alloys (at elevated temperatures) will favor the negative end of the scale (-300 mV to -350 mV), whereas units experiencing preboiler flow accelerated corrosion or high iron transport will favor the less negative end of the control range.

With the preceding chemistry tests and online instrumentation in Figure 8 (in main presentation) the recovery operator has the tools necessary for evaluating contamination sources from the makeup treatment system and the condensate system.

### **APPENDIX G: PREVENTIVE MAINTENANCE**

Preventive maintenance is critical to the proper operation of the makeup water treatment, condensate filtration and polishing, chemical feed, and monitoring systems. It is

particularly important to inspect and periodically replace valves that are routinely operated and that may cause chemistry upsets. For example, backwash water inlet valves on ion exchangers eventually will leak and can contribute to effluent contamination. Also, isolation valves for regeneration eventually can fail and cause massive contamination of acid or caustic into the treated effluent. Failures in collection laterals and resin traps in ion exchangers in the makeup or condensate plants also can allow significant amounts of resin to enter the boiler and cause significant boiler water pH depressions. All of the mechanical equipment should be evaluated for its failure potential. Preventive maintenance also includes resin sampling, analysis, and replacement in the makeup and condensate treatment systems. Finally, sample conditioning systems must be maintained to provide satisfactory sample temperatures and chemistry instrumentation requires routine calibration checks and maintenance to ensure accurate and reliable readings. A preventive maintenance program for the water treatment program should include the following areas:

- Makeup Treatment Equipment
- Condensate Filters/Polishers
- Sample Conditioning System
- Chemical Feed Equipment
- Deaerator and Boiler Inspections

For modern facilities which apply high doses of oxygen scavengers and have very low dissolved oxygen levels (<2 ppb), an evaluation (e.g., ultrasonic thickness testing) of the condensate/feedwater system in areas of possible flow accelerated corrosion (FAC) is advised. This is a form of localized erosion/corrosion which has resulted in severe thinning and failure of feedwater lines and other pressure parts. The most susceptible areas are locations with two-phase flow, high velocities, and turbulence. The classic location is in an elbow downstream of a throttling valve - although it has occurred in deaerator droplegs, heater drains, economizers, and feedwater lines in the utility industry. Similar types of failures have been noted downstream of boiler blowdown regulating valves in recovery boilers.

### **APPENDIX H: PERSONNEL TRAINING**

All procedures to be followed by personnel responsible for chemistry should be documented in a laboratory manual or similar format. Personnel training is essential, particularly following major changes in chemicals used, water treatment equipment, control limits or response procedures. Periodic refresher training is very desirable, even in the absence of changes in the program.

### **APPENDIX I: CHEMICAL CLEANING**

While chemical treatment programs are designed to minimize boiler tube deposits, deposits eventually do form

in nearly all recovery boilers either gradually or suddenly as a result of a major chemistry upset. As indicated earlier, once these deposits form, the potential for a variety of tube damage mechanisms increases greatly. Deposits in drum-type generation banks may be largely removed through removal of steam drum internals and hydrojetting of the tubes. However, screen, nose, roof, waterwall and floor tubes generally cannot be effectively cleaned by hydrojetting. Therefore, periodic chemical cleaning of boilers usually is performed to remove accumulated deposits. Figure I-1 summarizes the objectives of chemical cleaning.

#### Figure I-1 - Objectives Of Chemical Cleaning

- ◆ Safe And Timely Removal Of Waterside Deposits To Prevent Enhancement Of:
  - Fireside Corrosion
  - Waterside Corrosion
  - Overheating Of Tube Metal
- ◆ Cleaning Should Be Regarded As An Integral Part Of The Water Treatment Program
- ◆ Waterside Deposits In Waterwall Tubes Should Be Determined Every 1 To 2 Years

#### Determining the Need to Chemically Clean

Figure I-2 summarizes the criteria normally used to determine the need to chemically clean a boiler.

#### Figure I-2 - Cleaning Criteria

- ◆ Time
- ◆ Deposit Thickness
- ◆ Deposit Weight
- ◆ Deposit Composition
- ◆ Tube Failures

Traditionally, black liquor recovery boilers were cleaned at least every 10 years. However, longer and shorter intervals have been selected based on other cleaning criteria.

Deposit thickness can be determined in waterwall tubes by direct measurement with a micrometer or micrographic analysis on tube samples removed from the boiler. However, the deposit weight generally is more often used as the primary criteria for determining the need to clean boilers.

Common deposit weight removal methods for boiler tube samples are included in D3483, an ASTM procedure (58). The mechanical method of deposit removal is more accurate at low deposit weights and is considered more useful for long term trending of deposit weight accumulation rates. The glass-bead method of deposit removal in NACE Standard TM0199-99 yields comparable results as the mechanical method of deposit removal (90). One manufacturer of recovery boilers has stated that all recovery boilers should be cleaned when deposit weights reach 13-22 mg/cm<sup>2</sup> (12-20 gms/ft<sup>2</sup>) (59).

Figure D-1 (Appendix D) included typical locations where heavy deposits have been detected and tube samples removed on other boilers. Figure I-3 is a photograph of a tube removed from a recovery boiler on a polymer dispersant program. Although waterside deposition was minimal at locations which could be observed during visual inspections, buildup was significant at locations subject to high heat flux.

Figure I-3 - Localized Waterside Deposits



With the proliferation of composite tubes, there is an increasing resistance to routine collection of tube samples from the lower furnace. Increased monitoring and trending of tube metal temperatures and videoscopic inspection of tube interiors can be very useful in finding the locations of tubes with greatest deposit thicknesses. This can improve the representability of tube samples that are collected and minimize unnecessary tube sampling. Generation bank tubes, roof and front wall tubes, and some screen wall tubes often can be inspected videoscopically by removing steam drum internals. One facility has performed a videoscopic survey of the entire lengths of tube interiors from each type of circuit in a boiler and has started to videoscopically inspect the remaining length of tubes above and below locations where samples are collected during routine tube sampling to assess the representability of tube samples.

Deposits that contain large amounts of copper, hardness, carbon, or silica, can complicate the cleaning process - particularly when present in layers. Therefore, sometimes cleaning is recommended sooner to avoid more complicated cleaning procedures in a future cleaning. Also, deposits can become more adherent and more difficult to remove over time.

A chemical cleaning often is required following boiler tube failures. This may be to remove internal deposits and/or corrosion products or to precondition new tubes. If greater

than 10% of the tubes are replaced, chemical cleaning is advised.

Other criteria that can be used to determine the need to clean include the frequency and extent of excursions from permissible limits of boiler water chemistry and the frequency and degree of operation outside of design recommendations (60). Boilers generally will have a lower tolerance for deposits and be more prone to failure when operated above design conditions.

## Solvent Selection

Traditionally, hydrochloric acid with various additives was the most frequently used solvent to clean recovery boilers - as shown in Figure I-4 (61). It is a very aggressive, general solvent for removal of metal oxides, hardness salts and siliceous materials. Hydrochloric acid is inhibited to minimize attack on boiler steel. However, hydrochloric acid is very aggressive to stainless steel. For boilers with stainless steel overlay or composite tubes in the lower furnace, a leak in the upper furnace during a cleaning could be very detrimental to fireside surfaces contacted by the leaking acid.

### Figure I-4 - Chemical Cleaning Solvent

#### Common

- Hydrochloric Acid (5-7.5%), Ammonium Bifluoride (0.25-1.0%), Copper Complexor (0.3-1.5%) And Inhibitor (0.2%) Followed By Rinses And Neutralization With Soda Ash (1.0%)

#### Less Common

- Organics Removal Via Caustic Or Potassium Permanganate Boilout
- Ammoniated Citric Acid (3-6%) Or EDTA (4-8%) With Inhibitor (0.1-0.2%). After Iron Oxide Removal, Oxidants (And Sometimes Additional Ammonia) Are Added For Copper Removal And Passivation

If the waterside deposits consist mainly of iron oxide with lesser amounts of copper oxides, ammoniated chelants (EDTA, Citrate) are often used in the electric utility industry and sometimes in the pulp and paper industry to chemically clean boilers. The solvents are inherently less aggressive and are usually recommended to clean boilers that have experienced waterside hydrogen damage. Organic solvents also should be considered for boilers with waterside cracks or stress-assisted corrosion. Unfortunately, these solvents are slower and much more expensive. Hardness deposits also may be removed by EDTA, but the cleaning may require extended contact times.

Many recovery boiler cycles also can occasionally experience black liquor or other process organic leakage which results in organic deposits forming in the boiler (59,61). Organic buildup can result also from overzealous use of filming amines in efforts to reduce condensate corrosion (61). If these deposits are relatively fresh and soft, they frequently can be removed by using a caustic preboil prior to acid introduction. If organic deposition is allowed to

remain and bake onto tube surfaces, it becomes hard, heat-insulating and difficult to remove. Such deposits often can be cleaned from the boiler following a permanganate treatment.

## Procedures and Planning

A technical committee of TAPPI has published a document "Keys to successful chemical cleaning of boilers" (TIP 0416-06), that provides a general introduction to chemical cleaning processes (4). However, chemical cleanings can be an exceedingly complex process and some of the conditions listed in this document may not be appropriate for your facility (e.g., hydrochloric acid temperatures down to 120°F (50°C) (sic) often are inadequate to effect deposit removal) (4). Also, for boilers with heavy localized deposits (>50 mg/cm<sup>2</sup>), inspection of a tube specimen in an isolatable pipe loop should be considered to help to determine cleaning effectiveness during the cleaning process. More detail on chemical cleaning of boilers is provided in the technical reports on chemical cleaning published by the Electric Power Research Institute (60,62,63).

Chemical cleaning should be considered an integral and necessary part of the overall water treatment program. It is a nonroutine task requiring a great deal of work to satisfactorily accomplish its desired goals without endangering personnel or equipment. Mills should select contractors and consultants for these projects very carefully.

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