BASIC WATER TREATMENT OF STEAM BOILERS

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This is a brief discussion on low-pressure steam boiler chemistry. It provides dry kiln boiler operators the tools to maintain an efficient and effective boiler chemistry program. The main goal of this discussion is to provide these tools to operators so that they will be able to detect and prevent problems with their boilers and kilns preferably before they happen.

In order to fully understand what a given boiler needs for treatment, a basic study of its supply water must be done first. Three types of impurities exist in all supplies and can cause a wide range of problems in boilers and kilns. These impurities are suspended solids, dissolved solids, and dissolved gasses. Water picks up the impurities from the ground it contacts and the air through which it falls. The type of impurity depends on contact time, and stream velocity. The amount of rainfall and where the rain occurs on the watershed can and does result in changes in the character of the water throughout the year. Water supplies typically come from one of two sources, ground water or surface water. Generally, ground water contains more dissolved solids and less suspended solids and dissolved gases. Generally, surface water contains more suspended solids and dissolved gases and less dissolved solids.

Most problems due to impurities present in the water can be solved chemically, one way or another. It is usually most economical, however, to address the impurities by physical or mechanical means, using chemical treatment only to clean up the remaining traces left after physical treatment. Not only will this pre-treatment minimize chemical costs, it also has the difficult to measure benefit of improving a plant's reliability while simplifying operators' jobs. Operating kiln boiler plants without adequate pre-treatment can be compared to a high wire act without a net...one slip and its curtains.

Common Pre-treatment Methods Found in Dry Kiln Operations		
Suspended Solids	Dissolved Solids	Dissolved Gases
Filtration	Ion Exchange Softening	Deaeration
Clarification	Demineralization	Degasification
	Reverse Osmosis	Dealkalization

The optimum pre-treatment scheme for each plant must be worked out on an individual basis taking the entire system into account. Costs, maintenance requirements, environmental impact, and many other factors come into play.

In the Northwest it is not all that common to have a suspended solids problem with dry kiln boilers. However, the problem does exist. Suspended solids can cause corrosion and deposition problems in boilers and in kilns. Simple multimedia filters are a common way to remove suspended solids. A pressure vessel, filter bed of various sizes of gravel, sand, and anthracite coal is usually sufficient to reduce suspended solids to acceptable levels. Improvements to filter performance can be achieved through chemical means. Another way to remove suspended solids involves a settling basin or clarifier. Still water promotes particulate settling. The addition of coagulant and flocculent

chemicals speeds up and improves this settling process. The result is cleaner water for boiler makeup or other applications.

In an effort to address a dissolved solids problem, many dry kiln plants use water softeners to pre-treat boiler makeup prior to system entry. Many advantages to its use become apparent when the softeners function is understood. The main types of boiler scale are composed of calcium or magnesium, which can be readily removed in makeup water by softeners. Their removal dramatically reduces the possibility of boiler scale formation. Water softening can be performed by ion exchange, whereby favorable sodium ions are exchanged for unfavorable calcium and magnesium hardness ions by the ion exchange resin beads. Eventually, the softener resin bed exhausts (fills up with unfavorable ions), and must be regenerated, rinsing the unfavorable hardness ions to the drain and replacing them with sodium ions. The softener bed is again ready for service.

Similarly, if better dissolved solids control is required, another form of ion exchange may be employed. Demineralization is a method of choice for removal of nearly all dissolved solids for higher-pressure boilers that have tighter restrictions on boiler chemistry. Positively charged ions (cations) such as sodium, calcium, magnesium, and iron are exchanged for hydrogen ions, and negatively charged ions (anions) such as chloride, sulfate, carbonate, and silica are exchanged by hydroxide ions. Instead of salt, Demineralizers are regenerated with sulfuric or hydrochloric acid for cation beds, and sodium hydroxide for anion beds.

Reverse osmosis is yet another method for reducing dissolved solids from water supplies. It too reduces both positively and negatively charged ions but in a different way. Since RO is a process that requires much attention and usually has pretreatment of its own, it is rare in low-pressure dry kiln boiler operations.

To reduce corrosive dissolved gases from makeup water most plants use some variation of a deaerator. Deaerators exploit the physical properties of temperature and pressure to drive off dissolved gases. The warmer water gets the less carbon dioxide and oxygen can be dissolved. Once the gasses are forced out of solution they are vented off with a steady flow of steam. To improve a deaerator's performance a plant may need to increase the temperature and/or steam flow. Depending on the DA design, some other mechanical improvements may be required.

One way of reducing the corrosive gas, carbon dioxide in steam and condensate involves the use of a dealkalizer. Dealkalizers are yet another form of ion exchange. Like softeners they are regenerated with salt and often a combination of salt and sodium hydroxide. Dealkalizers exchange undesirable negatively charged ions mostly carbonates for desirable ions mostly chloride and some hydroxide. Carbonates break down in boilers to form carbon dioxide, which carries off with the steam. Carbon dioxide becomes very corrosive when it dissolves in condensate. Pitting is often evident in kiln piping where condensation occurs in systems where carbon dioxide is a problem. Keep in mind that the source of most carbon dioxide is not a dissolved gas in makeup water removable by deaeration. It comes as a dissolved solid associated with sodium and calcium as carbonates or bicarbonates in makeup water, which then transforms into carbon dioxide inside boilers. Deaeration can remove carbon dioxide in return condensate, but damage is already done in kiln and return condensate piping.

Specifically, there are a number of advantages to a properly managed boiler chemistry program. Boiler chemistry programs include not only chemical addition, but also pre-treatment equipment. Maximized equipment life, reduced maintenance costs, minimized down time, maximized safety, optimized chemical costs, minimized fuel costs,

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minimized water consumption, and minimized waste water are the main benefits. Equipment that is properly protected will last longest and will require the least amount of maintenance and down time. The same equipment is less likely to have catastrophic failures leading to safety concerns. Properly treated systems will also reduce chemical, fuel, and water consumption to a minimum. Reduced water consumption directly translates into further reduced fuel consumption since every gallon of water that enters the system requires energy to raise its temperature to turn it to steam.

As sentinels of the heart of dry kiln plants, boiler operators have control over two basic aspects of the chemical program; blow down and chemical feed. Blow down requirements are determined by the type and amount of impurities that exist in the makeup water. Blow down rates of course directly affect chemical feed rates. Therefore, a complete analysis of the raw and makeup water is the first step in establishing the correct program. From this analysis a qualified firm can determine the right operating parameters for the program.

The impurities found in the makeup water will build up in the boiler as the water turns to steam leaving most impurities behind. There are known maximum limits for these impurities, which can and will be surpassed without proper blow down. The maximum concentration allowable by the limits can be expressed as the maximum cycles for that water supply. Usually one impurity will reach its ceiling first, making it the limiting factor for that water supply and thus establishing a boiler's maximum cycles. When a material surpasses its solubility limit, it begins to form deposits or precipitate. The actual limits are not exact numbers for all plants and boilers but are best expressed by ASME or ABME guidelines (see chart below). Some of the impurities (calcium salts, etc.) begin to precipitate as a result of the higher temperature and pressure of a boiler environment. They either form deposits or react with treatment chemicals to form harmless materials that are removed through blow down. Calcium, for instance, reacts with phosphate at the proper pH to form hydroxyapatite, a harmless precipitate sludge (when dispersed) that falls to the bottom of the boiler where it can be removed through bottom blow down. When boiler water pH is not within the proper range, calcium reacts with phosphate to form harmful calcium phosphate scale. Other impurities such as silica and iron can be tied up by dispersants and chelants and remain suspended in the boiler water where they can be removed by continuous surface or bottom blow down. Left improperly treated silica and iron both can form harmful deposits.

ASME Guidelines for Water Tube Boilers						
Drum Pressure (psig)	Iron	Copper	Total Hardness	Silica	Total Alkalinity	Conductivity
0-300	0.100	0.050	0.300	150	*700	7000
301-450	0.050	0.025	0.300	90	*600	6000
451-600	0.03	0.020	0.200	40	*500	5000

* Total Alkalinity must not be allowed to exceed 10% of the Conductivity.

ASME Phosphate Treatment Guidelines (boilers below 600 PSIG)	
OH-Alkalinity	100-600ppm
Phosphate	30-50ppm
Silica	200 - (0.25x Boiler Pressure)
Total Dissolved Solids	2000-3000ppm

It is difficult to determine the true concentrations of many impurities in the boiler water because of their interactions with treatment chemicals and other impurities. Chlorides, however, are relatively unaffected by other materials in the boiler. When compared to the makeup water chloride concentration, boiler water chloride concentration will most accurately show the cycles of concentration of a boiler. Consequently, chlorides should be used to control boiler blow down. If ten cycles of concentration are permissible for a given boiler, then the concentration of chlorides should never exceed ten times that of the makeup water. For example, the makeup water chloride concentration is 10ppm so the boiler chloride concentration must never exceed 100ppm.

The only way to control the cycles of concentration in boilers is to remove (blow down) some of the highly concentrated boiler water. Makeup water replaces blow down and dilutes the remaining boiler water. Blow down is performed two ways; bottom blow down and surface blow down. Ideally, blow down should be done in proportion with steam production. If the entire blow down is being done manually, as with bottom blow down, it is important that operators monitor cycles closely and adjust frequency and length of time of blow down accordingly. This process can be very difficult to control cycles of concentration. A surface blow down does a much better job of keeping cycles leveled out, since a constant flow of blow down can be adjusted via a metering valve. In any case, the boiler water chloride level should be monitored to ensure the blow down rate is correct. If the chloride level is higher than the recommended maximum, more blow down is needed. If it is low, excess blow down is occurring, resulting in wasted chemicals, water, and heat energy. In some cases the chloride level never approaches the recommended maximum, even if little or no blow down is being done. Consequently, the boiler may have a vessel leak or a leak through its bottom blow down valve(s).

If a plant's steam production fluctuates like dry kiln operations do, the surface blow down stream can easily be set up to automatically compensate for the changes in required blow down rates. A steam grade solenoid valve or motor operated valve can be installed in the surface blow down line. The feed water pump circuit actuates the valve. As the steam load increases, the water level in the boiler falls more quickly and activates the feed water pumps more often and/or for a longer period of time. Consequently, the chemical addition pump(s) adjust feed rate(s) automatically. To fine-tune the blow down rate, a metering valve on the surface blow down line must be adjusted initially. Once the metering valve is adjusted properly, the system will remain quite stable. This configuration is known as proportionate blow down. Manual blow down then becomes primarily a sludge removal function and does not need to be varied to control cycles. A variation of this blow down control method includes the actuation of the blow down valve by a makeup water meter or makeup water valve. Since the steam production rate directly affects the makeup water requirements, the required blow down rate is also proportionate to the makeup water needed. As the amount of makeup increases, the water meter or valve actuates the chemical pumps more often. To visualize how much blow down is actually required, ten cycles of concentration means that one pound of blow down is required for every nine pounds of makeup water used, or 10% blow down rate. Twenty cycles would be one pound of blow down for every nineteen pounds of makeup water used, or a 5% blow down rate. Monitoring actual cycles is critical in minimizing water, chemical and fuel use. If cycles get too high, even proper levels of the best chemicals cannot guarantee deposits will not form. In this situation carryover may also occur, contaminating the steam and possibly damaging system components. Chloride testing is the only way to monitor cycles accurately.

With the right blow down rate established, chemical feed can be fine tuned by recipe changes or dosing pump setting changes to bring residual chemical concentrations into the proper ranges. Standard boiler chemical programs include sodium hydroxide

(caustic soda) for alkalinity, sodium sulfite for oxygen scavenging, some form of phosphate for scale prevention, phosphonates and synthetic dispersants for deposit control and/or removal. Also, various amines are employed for return condensate treatment, which prevent condensate line corrosion and ultimately corrosion product deposition in the boiler.

A variety of parameters should be tested to maintain good boiler chemistry control. Conductivity testing is used to monitor the amount of material dissolved in water by measuring its ability to conduct electricity. The more material dissolved in the water, the higher its conductivity will be. As a boiler approaches its maximum allowable cycles, it will also approach its maximum allowable conductivity. If a boiler water's conductivity gets too high, indicating excessive dissolved material is present, steam will start to have trouble escaping the water's surface. This phenomenon is due to increased water surface tension from higher dissolved solids concentrations. The boiler at this point will begin to prime, or foam and bounce, resulting in tiny droplets of boiler water carrying over with the steam. Good quality steam is essentially distilled water. Carryover reduces the BTU content of the steam resulting in excess fuel consumption and reduced kiln efficiency. Measuring condensate and boiler water conductivities are important for ensuring good steam quality and can expose mechanical problems with boiler and kiln operation.

Sodium hydroxide provides a highly alkaline environment in the boiler. This is about the only environment where water and steel get along well. Heat magnifies the normally corrosive effect water has on steel, since it speeds up chemical reactions. Maintaining the correct alkalinity range minimizes this highly corrosive effect of water. Alkalinity also plays a critical part in various chemical reactions in the boiler. Frequently, most of boiler water alkalinity comes from the addition of sodium hydroxide in the chemical program. Some of the alkalinity comes from naturally occurring alkalinity found in raw water supplies. If it is present naturally, it contributes to the required alkalinity in the boiler and decreases the amount of sodium hydroxide needed.

Alkalinity is typically measured as either P-Alkalinity (Phenylthalein Alkalinity) M-Alkalinity (Methyl Orange Alkalinity) or OH-Alkalinity (Hydroxide Alkalinity). P-Alkalinity is determined by a relatively simple titration procedure. OH-Alkalinity is determined by either using a modified version of the P-Alkalinity test, or by calculation using P and M-Alkalinity (2xP-M=OH). OH-Alkalinity is primarily the most important. However, P-Alkalinity is more convenient to test. If P-Alkalinity is in range, the OH-Alkalinity will be also. Boiler alkalinity is directly related to boiler pH so if the alkalinities are in range, the pH will be also.

Chloride, as discussed earlier, is used to monitor cycles of concentration and to control blow down rates. Makeup water and boiler water should both be tested to determine the cycles of concentration. Makeup water quality can change with time. For example, failing water softener has the potential to increase the chloride concentration in the makeup water. Along the coast seawater encroachment has the potential of dramatically changing makeup water chloride concentrations also. The procedure for testing both boiler and makeup water samples is the same except for one thing. The boiler water sample must be pH neutralized. The chloride test is most conveniently done on the same sample as the P-Alkalinity test for boiler water. This sample has already been neutralized with an acid titrant. The chloride test will not work properly on a high pH sample. (Note: OH-Alkalinity samples cannot be used for chloride testing. This test uses barium chloride, resulting in an incorrect high chloride reading.) The recommended chloride range for a boiler depends greatly on the makeup water chemistry.

Sulfite

Sulfite is used to consume dissolved oxygen in steam boiler systems. If dissolved oxygen is permitted to exist in the boiler, it attacks the steel in the boiler forming oxygen pits. This pitting causes serious damage and eventually tube failure. This is the most common form of corrosive attack in steam boilers. Dissolved oxygen can also flash out with the steam and cause corrosion throughout the condensate return system. Sulfite reacts with dissolved oxygen to form sulfate, thus making the oxygen unavailable to damage system metals. Sulfite is best fed into the feed water system as far upstream as possible. The optimum feed location is at the storage portion of a DA. A long distance in the feed water stream increases the reaction time of the sulfite with the oxygen decreasing the possibility of oxygen getting into the boiler. Consequently, much of the feed water system also gets protected.

Phosphates

Phosphates are used to react with calcium and magnesium hardness to produce controllable materials (hydroxyapatite and serpentine) removable by blow down. Phosphates should be added to low pressure boilers to maintain a residual of 30 to 60ppm as ortho-phosphate. Testing for phosphate in a boiler sample requires filtering out the phosphate precipitates already formed. Any calcium or magnesium present will consume the ortho-phosphate. The consumed phosphate can still show up on the tests giving false high readings. The benefit of softening boiler feed water becomes very evident once basic boiler water chemistry if fully understood. Hard makeup water requires enough phosphate to maintain the 30 to 60ppm residual in addition to that needed to neutralize all of the calcium and magnesium hardness in the boiler water. Soft makeup water only requires enough phosphate to maintain the same 30 to 60ppm residual. A boiler on soft makeup can be operated at higher cycles of concentration, thus requiring less blow down and less chemical treatment in general.

Dispersants

Phosphate precipitates (sludge) must be dispersed thoroughly to prevent them from baking on to the heat transfer surfaces of boilers. A variety of dispersants are used for this purpose and must be fed in a proper ratio to the phosphate treatment. Sodium lignosulfate, a brown organic substance, has been used in lumber mill boilers for many years. However, it has many limitations that the more modern synthetic dispersants and scale inhibitors do not have. The newer treatment chemicals available today have much greater capabilities but tend to be more expensive. The lignosulfate and some of the modern dispersants should not be used together since they can react, making both useless and possibly making an undesirable material. In most cases older treatment programs using lignosulfate should be converted to more modern programs using phosphonates and other dispersants and scale inhibitors.

Amines

Return condensate is naturally corrosive because of its purity. The pH of pure water is easily decreased in the presence of carbon dioxide. Carbon dioxide dissolves in the water to form carbonic acid. Oxygen readily dissolves in pure water also. Both low pH and dissolved oxygen lead to corrosion in any water system especially in the presence of heat. The amount of carbon dioxide in a dry kiln depends primarily on the amount of carbonates present in the makeup water. Various amines are used to neutralize the resulting carbonic acid in condensate causing the pH to stabilize at higher less corrosive

levels. The return condensate system is then protected from carbonic acid corrosion. Reducing corrosion decreases the amount of corrosion products that would normally return to boiler and form deposits. These deposits can be the most difficult to remove. An amine or blend of amines must be selected to meet the needs of each system. The choice of amines depends upon the length of the steam lines and their configurations (T's etc.). Amines are rated through distribution ratios (DR's). The higher the DR the further the amine travels. A high DR amine has a great affinity for being in the steam phase. A low DR amine has some affinity for staying behind in the water phase (in the boiler). The lower the DR the more it recycles in the system. In a smaller dry kiln operation a lower DR amine is usually most economical as a result. Special amines known as filming amines are used to coat the inside of the return condensate system further protecting them from corrosion.

Neutralizing amines should be fed at a rate sufficient to produce a return condensate pH of 8 to 9 for best results. The exact feed rate depends on the percent of condensate return since higher return rates mean less makeup, the primary source of carbon dioxide. A higher return rate also means better recycling of the amine already fed into the system. As a result, less amine has to be fed to replace what is lost. Amines may be fed in several locations depending on the configuration of the system. They may be fed directly into the boiler, the steam header, or into various strategic steam line locations. Some recycled amine will be lost in a DA since some steam is vented from DA's. Adding the amine to the steam header downstream of steam line to the DA makes economical sense.

Chemical feed is best done in proportion with water use. Like blow down control, makeup or feed water flow rates can be used to actuate chemical feed systems. This chemical feed technique automatically compensates for changes in steam load giving stable chemical treatment control in the system. One of the simplest ways to employ this technique is to have the feed water pumps actuate the chemical pump(s). Once blow down and chemical feed rates are correct and stable, testing should be done regularly to monitor any changes that may occur in the system. Any chemistry changes may be indicators of mechanical changes in the system. Once the relationship of boiler chemistry is fully understood, an attentive operator can diagnose problems to his plant by noticing changes to boiler chemistry. For example, a system set up on proportional control normally operates at 75% condensate return with fairly stable chemistry. One day an operator notices his cycles of concentration increase, but the other chemistry stays in line. He makes sure the chloride tests are accurate on the boiler and makeup water. He notices, however, his chemical usage has increased. Finally, he determines that he must be losing more condensate (now only about 60%) possibly through a new leak or through a change in lumber conditioning procedure, because of the mathematical relationship that exists between cycles of concentration and condensate return rate. Given the same blow down rate, cycles of concentration will increase with a decrease in condensate return. Makeup water with dissolved solids must be added to replace lost (fairly pure) condensate. As more dissolved solids are added to the boiler the cycles of concentration increase. The operator may have also noticed a decrease in condensate pH. This would have been due to the increase in carbonates added to the system through increased makeup requirements and through a decrease of recycling amine. Many other scenarios are likely to occur in dry kiln operations and can usually be traced through attentive chemistry monitoring. When these changes are noticed when they first happen, operators can quickly prevent a variety of problems and increasing chemical costs.

Mathematical Relationships for Boiler Chemistry Programs

Feed Water   = Makeup Water + Condensate Return

Makeup Water   = Blow Down + Condensate Loss

Boiler Lay-up Procedure Wet Storage

Wet lay-up is used when the boiler will be out of service for shorter periods of time. The boiler can be brought back into service quickly when laid up wet.

1. Fill the boiler to its normal operating level, preferable with deaerated feed water.
2. The water should be boiled with the unit vented to the atmosphere to purge the boiler of any excess air.
3. Add enough catalyzed sodium sulfite to achieve a residual of at least 100ppm as SO_3. This will require the addition of approximately 1.0 to 1.5 pounds of sodium sulfite per 1000 gallons of water in the boiler.
4. Feed sufficient caustic soda (sodium hydroxide) to establish a pH of at least 11.0 or a P-Alkalinity of 500 to 600ppm as calcium carbonate. The quantity of caustic will depend on the alkalinity of the fill water.
5. Before the unit has cooled to the point where a vacuum has been drawn, completely fill the boiler with deaerated feed water.
6. Tightly close all connections and apply a small positive pressure to compensate for the vacuum that will develop as the unit cools to room temperature. This can be achieved by using the feed water pump. As and alternative to applying a backpressure, it is possible to maintain a head or reservoir to serve the same purpose. Connecting a clean 55-gallon drum to the vent line or other available fitting atop the boiler will does this. As the boiler is filled, the drum collects the overflow. Then, as a vacuum develops because of cooling, the water in the drum enters the boiler and keeps it full. Additional water added to keep the drum filled should be treated with sulfite (1oz per 50 gallons) and caustic (approximately 1.5 oz per 50 gallons).
7. The boiler should be tested weekly as long as the unit is in storage. Sulfite and caustic should be fed as required to maintain the recommended levels. When more chemical is added, it is desirable to circulate the boiler water for a short time by means of an external pump.
8. For startup, drain the boiler to the normal operating level. Initiate the feed of regular boiler water treatment chemicals as soon as the boiler is placed in service.