AN ENERGY AUDITING COMPANY

Boiler Feed-Water Treatment

(Note. You will see the thumbs up TIPS GUY on this page. Just place your mouse pointer over the image.)

Even the most simple of water powered machinery requires some sort of water treatment, before the water is admitted into the working parts of the machine. Take for example, the water wheel of this beautiful 18th century water mill. Prior to the water running onto the wheel, the surface of the water is "skimmed" by a simple board and grill, in order to remove floating debris. A simple but highly effective form of mechanical water treatment.

Different machines require different techniques and levels of treatment, and with this in mind, we move onto the subject of boiler feed-water treatment. The analysis and treatment of boiler feed-water is a task the plant engineer would normally leave to a qualified contractor, since the whole subject of boiler feed-waters, and their treatment is one for the chemist, rather than the engineer.
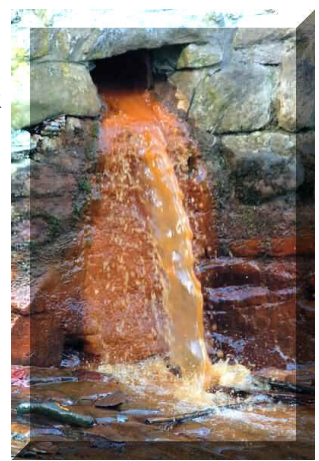
However, the plant engineer, or engineering manager has to understand the cause, and effect scenario regarding feed-water impurities, and their potential effect upon plant equipment and operations.

The issues and techniques discussed below, are quite applicable to drum type boilers operating in manufacturing plants, at pressures up to about 300 psi. Generally speaking, the higher the boiler pressure, the more rigorous the water treatment must be..

COMMON BOILER FEED-WATER CONTAMINANTS

IMPURITY	RESULTING IN	GOT RID OF BY	COMMENTS
Soluble Gasses			
Hydrogen Sulphide (H_2S)	Water smells like rotten eggs: Tastes bad, and is corrosive to most metals.	Aeration, Filtration, and Chlorination.	Found mainly in groundwater, and polluted streams.

Carbon Dioxide (CO_2)	Corrosive, forms carbonic acid in condensate.	Deaeration, neutralization with alkalis.	Filming, neutralizing amines used to prevent condensate line corrosion.
Oxygen (O_2)	Corrosion and pitting of boiler tubes.	Deaeration & chemical treatment with (Sodium Sulphite or Hydrazine)	Pitting of boiler tubes, and turbine blades, failure of steam lines, and fittings etc.
__Suspended Solids__			
Sediment &Turbidity	Sludge and scale carryover.	Clarification and filtration.	Tolerance of approx. 5ppm max. for most applications, 10ppm for potable water.
Organic Matter	Carryover, foaming, deposits can clog piping, and cause corrosion.	Clarification; filtration, and chemical treatment	Found mostly in surface waters, caused by rotting vegetation, and farm run offs. Organics break down to form organic acids. Results in low of boiler feed-water pH, which then attacks boiler tubes. Includes diatoms, molds, bacterial slimes, iron/manganese bacteria. Suspended particles collect on the surface of the water in the boiler and render difficult the liberation of steam bubbles rising to that surface.. Foaming can also be attributed to waters containing carbonates in solution in which a light flocculent precipitate will be formed on the surface of the water. It is usually traced to an excess of sodium carbonate used in treatment for some other difficulty where animal or vegetable oil finds its way into the boiler.
__Dissolved Colloidal Solids__			
Oil & Grease	Foaming, deposits in boiler	Coagulation & filtration	Enters boiler with condensate
Hardness, Calcium (CA), and Magnesium (Mg)	Scale deposits in boiler, inhibits heat transfer, and thermal efficiency. In severe cases can lead to boiler tube burn thru, and failure.	Softening, plus internal treatment in boiler.	Forms are bicarbonates, sulphates, chlorides, and nitrates, in that order. Some calcium salts are reversibly soluble. Magnesium reacts with carbonates to form compounds of low solubility.
Sodium, alkalinity, $NaOH, NaHCO_3$, Na_2CO_3	Foaming, carbonates form carbonic acid in steam, causes condensate return line, and steam trap corrosion, can cause embrittlement.	Deaeration of make-up water and condensate return. Ion exchange; deionization, acid treatment of make-up water.	Sodium salts are found in most waters. They are very soluble, and cannot be removed by chemical precipitation.
Sulphates (SO_4)	Hard scale if calcium is present	Deionization	Tolerance limits are about 100-300ppm as $CaCO_3$
Chlorides, (CI)	Priming, i.e. uneven delivery of steam from the boiler (belching), carryover of water in steam lowering steam efficiency, can deposit as salts on superheaters and turbine blades. Foaming if present in large amounts.	Deionization	Priming, or the passage of steam from a boiler in "belches", is caused by the concentration sodium carbonate, sodium sulphate, or sodium chloride in solution. Sodium sulphate is found in many waters in the USA, and in waters where calcium or magnesium is precipitated with soda ash.
Iron (Fe) and Manganese (Mn)	Deposits in boiler, in large amounts can inhibit heat transfer.	Aeration, filtration, ion exchange.	Most common form is ferrous bicarbonate.
Silica (Si)	hard scale in boilers and cooling systems: turbine blade deposits.	Deionization; lime soda process, hot-lime-zeolite treatment.	Silica combines with many elements to produce silicates. Silicates form very tenacious deposits in boiler tubing. Very difficult to remove, often only by flourodic acids. Most critical consideration is volatile carryover to turbine components.

THE BOILER DOES NOT A STEAM SYSTEM MAKE

Boiler feed-water consists of two components 1. Make-up water, 2. Condensate return. When discussing boiler feed-water treatment with potential contractors, the engineering manager should ensure that the contractor considers the plant steam installation as a complete system, of which the boiler is only a part. For example, in the polymer industry, the steam system metallurgy may consist of copper (heat exchangers), black iron (steam lines and distribution), aluminum (tooling and molds), carbon steel (boiler tube material), and tool steel (tooling and molds).

The subject of boiler feedwater treatment is a subject about which volumes have been written. Let's briefly consider the two major issues of:

- Corrosion (Water-side, and Fire-side)
- Scaling

WATER-SIDE CORROSION

Corrosion, or chemical action leading to the actual destruction of the boiler metal, is due to the solvent or oxidizing properties of the feed water. It results from the presence of acid, either free or developed in the feed, the mixture of air with feed water, or as a result of galvanic action. Developed acid can occur with waters not naturally acid. They become so at high temperatures, as when chloride of magnesia decomposes with the formation of free hydrochloric acid; such phenomena becomes much more serious with increasing pressure and temperature. In boilers corrosion takes several forms:-

- Pitting, which consists of isolated spots of active corrosion which does not attack the boiler as a whole.
- General corrosion, produced by naturally acid waters, and where the amount is so uniform and continuous, that is becomes difficult to estimate the amount of metal eaten away.
- Grooving, which, while largely a mechanical action which may occur in natural waters, is intensified by acidity.

Water-side corrosion takes place between the surface of the boiler tube in contact with the boiler water. Depending upon the method of boiler construction, this may be either on the internal, or external surface of the boiler tubes. Dissolved oxygen in boiler feed-water attacks boiler tubing, heat exchangers, pre-heaters, and economizers. Pits or corrosion pockets form, and may eventually grow large enough, penetrate the metal, and force a complete plant shut-down. The oxygen in the boiler feed-water becomes extremely aggressive when heated, in addition to boiler tube corrosion, further damage may occur to steam and mud drums.
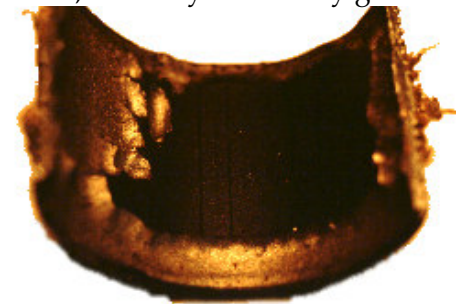
Dissolved oxygen in boiler feedwater intensifies the corrosion of boiler tubing, by acting as a depolarizer agent, and accepting free electrons liberated from the surface of the boiler tubing, and is instrumental in determining the intensity of waterside corrosion of boiler tubing.

$$Fe - 2e ---->Fe^{2+}$$

$$O_2 + 2H_2O + 4e -------->4OH^-$$

$$Fe^{2+} + 2OH^- --------> Fe(OH)_2$$
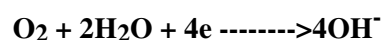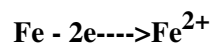
Oxygen corrosion causes extensive localized destruction of of the metallic surface of the boiler tubing, eventually leading to "pitting". This type of corrosion generally occurs at pH levels equal to or greater than pH 7. At ph <7 in the presence of acidic boiler waters, the corrosion becomes uniform in nature.

Depolarization

Depolarization is galvanic electrode process which diminishes polarization, i.e. it intensifies electrochemical corrosion. Depolarizers are chemical agents that contribute to this process by binding

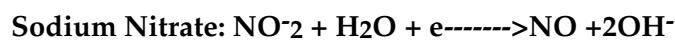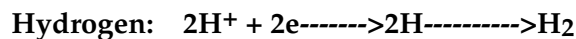free electrons. In order for electrochemical corrosion to commence, three conditions have to be satisfied.

- A galvanic pair must be established, i.e. two metals having different electrode potentials.
- A electrolyte in contact with the galvanic pair.
- Depolarizers must be present.

How can a galvanic pair of electrodes be present in the boiler tubing?

The boiler tubing material is not uniform in chemical composition throughout, and numerous minute galvanic cells are formed over the surface area of the boiler tubing, with the boiler water acting as an electrolyte. If one area of the tubing is more negative than the other, then electrochemical attack takes place in the area concerned, and destruction of iron from the anode occurs. These localized areas of corrosion are often referred to as "pits" or pitting.

In addition to dissolved oxygen as a depolarizing agent there are:

$$\text{Hydrogen:} \quad 2H^+ + 2e \text{------->} 2H \text{---------->} H_2$$

$$\text{Sodium Nitrate:} \quad NO^-_2 + H_2O + e \text{------->} NO + 2OH^-$$

Nitrates appear in boiler feedwater due to the oxidation of ammonium ions resulting from bacterial and organic surface contamination of pipelines, and mechanical filters. Periodic chlorination of bacteria contaminated pipelines should be carried out in order to eliminate this potential source of boiler tube corrosion.

$$NH^+_4 \text{--------->} NO^-_2 + NO^-_3$$
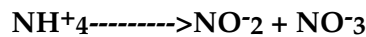
Another major source of corrosion in the condensate return piping is the presence of carbonic acid in the condensate. Carbon dioxide dissolved in water liberates H^+ ions that attacks metal.

$$CO_2 + H_2O \text{<==>} H_2CO_3 \text{<==>} H^+ + HCO^-_3$$

Carbon dioxide corrosion does more damage to condensate and equipment pipelines, than boiler tubing in contact with softened water, or "natural water". Natural and softened water contains quantities of HCO^-_3 which tend to to neutralize some of the H^+ ions.

$$HCO^-_3 + H^+ \text{<=====>} H_2CO_3 \text{<======>} H_2O + CO_2$$

The water borne (softened/natural) HCO^-_3 ions will favor equilibrium on the right and deter CO_2 dissolution in water. Therefore CO_2- corrosion will not be present in boiler tubing and equipment pipelines.

The same cannot be said of metallic pipelines and equipment in contact with condensate, which is very susceptible to CO_2 attack, since carbon dioxide rapidly dissolves in the condensate because of the absence of bicarbonate ions in the condensate water.

Controlling the oxygen in the boiler feed-water is achieved by both mechanical means, and chemical means.

The Mechanical Deaerator

The removal of dissolved gases from boiler feedwater is an essential process in a steam system. Carbon dioxide will dissolve in water, resulting in low pH levels and the production of corrosive carbonic acid. Low pH levels in feedwater causes severe acid attack throughout the boiler system. While dissolved gases and low pH levels in the feedwater can be controlled or removed by the addition of chemicals, it is more economical and thermally efficient to remove these gases mechanically. This mechanical process is known as deaeration and will increase the life of a steam system dramatically.
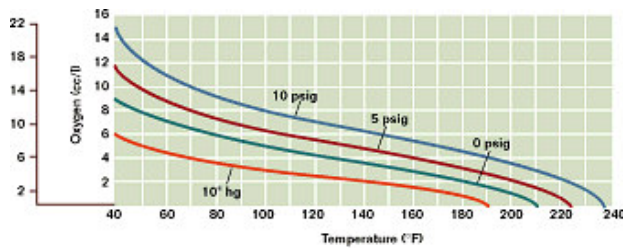
Deaeration is based on two scientific principles. The first principle can be described by Henry's Law. Henry's Law asserts that gas solubility in a solution decreases as the gas partial pressure above the solution decreases. The second scientific principle that governs deaeration is the relationship between gas solubility and temperature. Easily explained, gas solubility in a solution decreases as the temperature of the solution rises and approaches saturation temperature. A deaerator utilizes both of these natural processes to remove dissolved oxygen, carbon dioxide, and other non-condensable gases from boiler feedwater. The feedwater is sprayed in thin films into a steam atmosphere allowing it to become quickly heated to saturation. Spraying feedwater in thin films increases the surface area of the liquid in contact with the steam, which, in turn, provides

more rapid oxygen removal and lower gas concentrations. This process reduces the solubility of all dissolved gases and removes it from the feedwater. The liberated gases are then vented from the deaerator. Correct deaerator operation requires a vessel pressure of about 3-4 psi above atmospheric, and a water temperature measured at the storage section of 8 degrees Fahrenheit above the boiling point of water at the altitude of the installation. There should be an 18-24 inch steam plume from the deaerator vent, this contains the unwanted oxygen and carbon dioxide. The following parameters should be checked during each shift in order to ensure the correct operation of the deaerator.
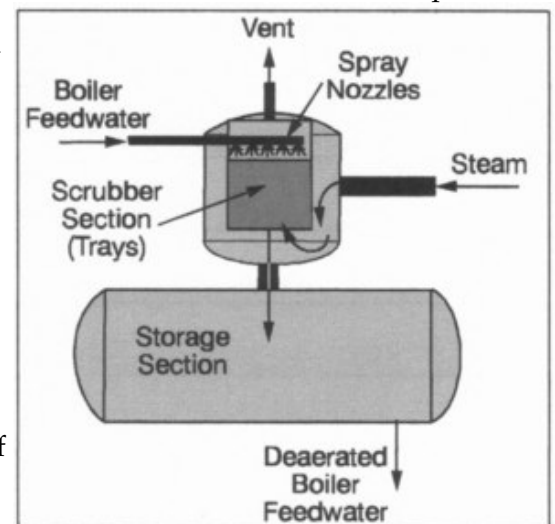
- Deaerator operating pressure

- Water temperature in the storage section

- 18-24 inch steam plume visible at the deaerator vent

- Dissolved oxygen level in the boiler feedwater, should be between 7-20 ppb, depending upon the deaerator type.

At this stage, I would like to mention the vacuum deaerator. The above mentioned principles of deaeration operation still apply. However, the process is carried out in a semi-vacuum, i.e. at a pressure less than atmospheric pressure. This technique is employed for small capacity, low pressure boilers, operating at a temperature less than 212 degrees Fahrenheit (373K). The saturation temperature of water at 1 atmosphere pressure is 373K, water at a lower pressure will boil at a lower temperature. Hence the partial vacuum inside the deaerator is required in order to maintain the saturation temperature at a lower level. The amount of vacuum required will be a function of the deaerated water temperature.

From the descriptions of deaerator operation appearing above, it is obvious that mechanical deaerator requires steam to be supplied from the boiler in order to function. This has an energy impact, since steam that would normally be used for process requirements, is now used for water treatment purposes. What is the magnitude of this "parasitic" steam load?

Steam injected into the deaerator provides the physical stripping action, and heats the returned condensate and boiler make-up water to saturation temperature. Most of the steam will condense into the deaerator assembly, but approximately 5% to 14% has to be vented to atmosphere in order to carry away the oxygen and carbon dioxide from the boiler feed-water. Good thermal design practice should allow for the steam required to heat the incoming make-up water to saturation temperature, plus the amount vented to atmosphere with the non-condensable gases. The calculation should be made using the minimum expected temperature for the boiler make-up water. The venting rate will be a function of the deaerator type, its size (rated feed-water capacity), and the amount (flow) of make-up water. The venting rate will be at a maximum, with the introduction of cold, oxygen rich make-up water.

A modern two stage deaerator can reduce dissolved oxygen concentration to less than 0.005 cc/liter (7 ppb), and completely eliminates the carbon dioxide concentration.

OXYGEN, THE KNOCKOUT PUNCH

Just a word here concerning oxygen scavengers. A dissolved oxygen level of 5pbb or lower, is required in order to prevent corrosion in most high pressure (>150psi) boilers. The final traces of oxygen can be removed from the feed-water with a chemical oxygen scavenger. The most common scavenger is sodium sulfite, Na_2SO_3 which oxidizes to sodium sulphate by chemical reaction with the dissolved oxygen in the feed-water.

$$2Na_2SO_3 + 0_2 ----> 2Na_2SO_4$$

As previously mentioned, the last remaining traces of oxygen in the boiler feedwater can be removed by chemical treatment with oxygen scavengers. In this next section we will explore the costs involved using sodium sulfite Na_2SO_3 as the scavenger agent. Before we embark upon the examination of dosage economics, I wish to draw the readers attention to the subtle difference between deaeration and deoxygenation:

- Deaeration is the removal of both O_2 and CO_2 by thermal degasification methods

- Deoxygenation is the removal of O_2 only, using chemical techniques

Dosage Economics

Let's start by stating that:

- 7.88 ppm of sodium sulphite is required to remove 1ppm of dissolved oxygen

However, the above figure assumes a pure sodium sulphite. In the real world, the purity of sodium sulfite available varies from one source to another. Purchasing a 93% pure sodium sulphate is relatively easy. Therefore, a correction factor needs to be applied to the dosage level to compensate for the purity level.

- The real world dosage level of sodium sulfite required to remove 1ppm of dissolved oxygen is 10ppm of 93% pure sodium sulphite.

Current USA prices for sodium sulfite in quantities of 100+ fifty-pound sacks is about $ 0.45 USD per pound. Assuming 93% purity, then the effective price of useable sodium sulphite is about $0.5 USD per pound.

We will now convert between pounds per gallon and parts per million"

- **10ppm sodium sulfite = 0.00009 lbs. Of sodium sulfite per gallon of water.**

We now introduce an old friend, namely, boiler horsepower (BHP), [CLICK HERE] to learn more about boiler horsepower and evaporation rates.

We have to relate our dosage to boilers, and to do this we will use the following:

- 1 BHP with an evaporation rate of 0.07 gallons of water per minute.
- 10ppm of sodium sulfite required for every 1ppm of dissolved oxygen to be removed.

Using the above figures, our treatment cost per boiler horsepower, per 1ppm of removed oxygen, per minute of boiler operation is :-

(0.07 x 0.00009) x 0.5 = $0.0000035 USD per ppm/per bhp/per min

I know that this sounds like a bit of a mouthful! But lets apply this idea to a real world example:

- Your have a 1000 hp boiler
- Sodium sulfite cost is $ 0.5 USD/lb. (93% corrected)
- The measured dissolved oxygen level in your boiler feedwater is 15ppm
- You want to reduce the level of dissolved oxygen to 0ppm

Then:-

$$60 \times \{](1000 \times 0.07 \times 0.00009) \times 0.5] \times 15\} = 2.84 \text{ USD per hour}$$

or

8,760 x 2.84 = $24, 878 USD per Year (Continuous Operation)

At this point, I would like to pass on a simple tip for dealing with water treatment contractors.

- In the absence of any firm data from the plant-engineering group, the water treatment contractor will always base quoted the scavenger costs on the amount of chemicals required to completely eliminate the dissolved oxygen in the boiler feedwater.
- You should always provide the water treatment contractor with the boiler operating hours per year, otherwise the contractor will assume a continuous operation of 8,760 hours per year.

Let us now re-examine these costs in a more professional manner:-

- The plant-engineering group has measured the dissolved oxygen content in the boiler feed-water at 15ppm.
- The plant engineer requires the dissolved oxygen level in the boiler feedwater to be reduced to 5ppm. ie 10ppm reduction.
- The plant production manager has scheduled the year's plant operations for 270 day 24/7 operations.

Revised Scavenger Costs:

$$60 \times \{](1000 \times 0.07 \times 0.00009) \times 0.5] \times 10\} = \$1.89 \text{ USD per hour}$$

or

6,480 x 1.89 = $12,247 USD per year 270 day 24/7 Operation

Having now determined the hourly dosage cost, the next task is to determine the amount of sodium sulphite to be added hourly to the BFW (boiler feedwater). To do this, divide the hourly treatment cost by the per pound price of sodium sulfite (93% corrected) :

$$1.89/0.5 = 3.78 \text{ lbs/hr.}$$

For a 24 hour period prepare an aqueous solution as follows: Using deoxygenated water dissolve 91 lbs of sodium sulphate to form a 5% aqueous solution. Store the prepared solution in a sealed container with minimum airspace above the surface of the solution. This will now be your daily stock solution, to be introduced into the boiler feedwater after deaerator.

The above example should demonstrate the need for a company to be in control when it comes to defining performance and specification criteria when dealing with water treatment contractors. If you have no idea of your required specifications and parameters, then be prepared to pay…

In closing out this section, just a word about combined deaerator and chemical scavenging. The reader must keep in mind that boiler water treatment costs, are a major contributor to life cycle costs of boiler plant operations, and anything that done to reduce water treatment costs will have a very favorable impact upon long term operational costs. Using a mechanical deaerator and a chemical oxygen scavenger is the most cost effective long term solution.

However, you should be aware that at very high boiler pressures, and temperatures, sodium sulphite becomes unstable, decomposes, and becomes ineffective as a deoxygenation agent.

$$Na_2SO_3 + H_2O \longrightarrow 2NaOH + SO_2$$

Hydrazine (*Hydrazine* N_2H_4 *requires careful handling.*)

Health Advisory: [CLICK HERE] for complete information concerning Hydrazine

Hydrazine is an effective oxygen scavenger, is very soluble in water, and reacts with dissolved oxygen.

The most widely used hydrazine oxygen scavengers are

- Hydrazine sulphate $N_2H_4 . H_2SO_4$

- Hydrazine hydrate $N_2H_4 . H_2O$

Hydrazine Sulphate

Is a solid, not very soluble in cold water, and is acidic.

- Temperature issues, hydrazine sulphate is effective as an oxygen scavenger only at water temperatures, equal to or greater than 373K.

- pH issues, at pH <7 hydrazine sulphate will fail to inhibit corrosion, and may even intensify it. At pH 9-9.5, and at a temperature of about 373-385K, a dosage of hydrazine above 20 micro-gram/kg will eliminate all dissolved oxygen, in about 3-5 seconds.

- Hydrazine Sulphate oxygen scavenging should only be used with drum type boilers. Drum boilers have blowdown facilities. TDS levels should be monitored more rigorously when using hydrazine sulphate as an oxygen scavenger, since TDS levels may increase with the formation of ferrous sulphate.

Hydrazine Hydrate

Hydrazine hydrate is normally used in "once thru" boilers, because, upon decomposition it leaves no solid residues. Therefore, having no affect upon the total dissolved solids (TDS).

$$N_2H4 + O_2 \longrightarrow N_2 + 2H_2O$$

As previously mentioned, hydrazine requires careful handling and storage. However, there are other spin-offs, in addition to hydrazine's ability as an oxygen scavenger. These are the reduction of Fe oxides and Cu as by products of metallic corrosion.

- Reducing iron oxides $6Fe_2O_3 + N_2H4 \longrightarrow 4Fe_3O_4 + 2H_2O$

- Reduction of copper $2CuO + N_2H4 \longrightarrow 2Cu + N_2 + 4H_2O$

As a finale, hydrazine hydrate reduces ferric hydroxide to ferrous hydroxide, and in the process inhibits nitrate corrosion in high pressure boiler installations.

$$4Fe(OH)_3 + N_2H_4 \longrightarrow 4Fe(OH)_2 + 4H_2O$$

In closing out this section, every pant engineer worth his "salt" must understand that chemical oxygen scavengers alone, cannot economically substitute for the function of a well designed and maintained deaerator.

FEED-WATER acidity levels

As previously mentioned boiler feed-water consists of two components, make-up water, and condensate returned from the plant processes. However, it is not unusual to see company boiler room personnel measuring the pH of the incoming make-up water supply only. Any meaningful measurement must taken from the output of the deaerator, or at the suction side of the boiler feed-water pressure pump. Any measurement of boiler feed-water indicating a pH of less than 8.5, then the feed-water should be considered as acidic. Possible sources of contamination to be considered, but not limited to:

- No deaerator installation.
- Poorly maintained deaerator
- Insufficient oxygen scavenging agent
- Contamination of condensate by cooling tower

In closing out this section concerning corrosion, there are some important points to consider:

- It is crucial that a suitable consultant, or water-treatment company be engaged. Such organizations will be able to analyze the water used in a boiler and steam system, and make recommendations for additives, or treatment.
- Include boiler feed-water specifications in your plant QA programs, and by monitoring, ensure that the correct chemical balance is maintained. This task is usually undertaken by the water-treatment contractor, in cooperation with the plant QA authority.
- Ensure that boiler room personnel are provided with portable handheld pH testers, and monitor boiler feedwater pH once per shift. Modern pH testers make this chore, simple, easy, and above all, unambiguous. There is no place in the 21st century for 19th century litmus paper testing methods for boiler feed-water pH.

ABOUT pH

Acidity and alkalinity is determined by the number of ions found in the water. An ion is a positively charged atom or group of atoms. If there is an excess of hydrogen ions H + (that is, positively charged hydrogen atoms), then water is said to be acid. If on the other hand there is an excess of the negatively charged hydroxyl ion (OH -), then an alkaline condition is said to exist.
The pH scale, as used by its originator Sörensen, expresses the concentration of positively charged hydrogen ions as the "logarithm of the reciprocal of the normality of free hydrogen ions." Mathematically written this means:

$$pH = \frac{1}{\log_{10} {}^{+}H \text{ ion concentrations in gram equivalents per liter}}$$

The scale is usually used on a range from pH 0.0 to 14-0 with three points of interest:

- pH of 0.0, the lowest point on the scale, represents a solution normal in hydrogen ions, that is to say, the strongest acid.

- pH of 7.0 is the middle or neutral point at which there is an equal number of hydroxyl and hydrogen ions.

- pH of 14-0, the strongest alkaline solution, means the solution is normal in hydroxyl ions.

 When pH is written as "pH 7-0," it is read, as "the pH is 7-0." To say that the pH is getting higher means that the solution is becoming more alkaline as the pH gets lower the solution becomes more acid.

The symbol pH itself has an interesting history. Sorensen, the first to use this symbol, proposed the use of the negative power of 10, or a power of 10 p where p stands for any negative number. the symbol was to refer to the "power of hydrogen" so the symbol H for hydrogen was added. Since all chemical symbols are capitalized in the first letter, the symbol became pH 10. this was reduced to merely pH, though actually the H should be inferior to the p, as pH.

There are several methods of measuring the pH, or hydrogen-ion concentration of a solution. All methods are easily categorized into two broad groups: Electrometric and calorimetric. Electrometric methods, by use of a "pH meter," merely measure the ability of a given liquid to conduct an electric current. These methods are extremely accurate. Colorimetric methods require the addition of a dye, which varies in colour with the pH, and comparison with a fixed standard, either electrically in a "calorimeter" or by the eye. Several inexpensive pH-testing sets are available from numerous sources, they are inexpensive, and a vital tool in ensuring correct boiler house operations.

SO..you have.. or do none of the above!!

I have been in many small to medium size factories in this region, where there is absolutely no attention paid to the issue of water-side corrosion. However, most factories do treat their boiler feed-water to prevent scale formation. In such cases, all that is available is a condensate return tank, vented to atmosphere, into which is introduced the boiler make up water, and condensate returned from the process.

If the condensate return tanks are vented to the atmosphere, and don't have vacuum breakers, the cooling and pumping of the condensate can result in the addition of atmospheric oxygen into the condensate return system resulting potential for oxygen pitting corrosion of the boiler tubes. In addition, there is insufficient scrubbing of carbon dioxide from the returned condensate, the resulting destruction of the condensate return systems, and high failure rate of steam traps, results from the uncontrolled build up of carbonic acid in the condensate. The pH level of returned condensate should be checked once per shift, a reading of below pH 7.5 is indicative of acidic condensate, and excessive levels of carbonic acid in the condensate.

Another related issue, very applicable to the polymer industry concerns aluminum tooling, which is alternately steam heated and water cooled. This operating condition can lead to failure of the alloy by cracking under the combined action of corrosion and stress, both residual and applied. This phenomenon is called "stress corrosion failure".

Some of the 7000, and 2000 aluminum alloys used in the construction of tooling dies, are susceptible to stress corrosion failure. Thermal stress in the presence of acidic (carbonic acid) condensate, can precipitate stress corrosion failures of these aluminum tooling alloys.
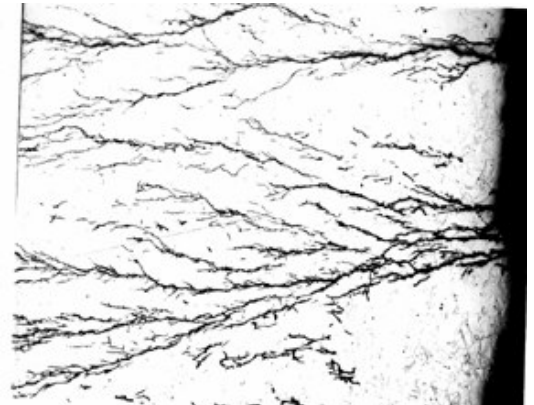
SCALING OF BOILER TUBES

Scale is formed on boiler tube heating surfaces by the depositing of impurities in the feed water in the form of a more or less hard adherent crust. Such deposits are due to the fact the water loses its soluble power at high temperatures or because the concentrations become so high, due to evaporation, that the impurities crystallize and adhere to the boiler surfaces. The opportunity for the formation of scale in a boiler will be apparent when it is realized that during a months operation of a 100 horse power boiler , 300lbs of solid matter may be deposited from

water containing only 7 grains per gallon, while some spring and well waters contain sufficient to cause a deposit of 2,000lbs. *(58,381 grains = one US gallon)*

The salts usually responsible for such incrustation are the carbonates and sulphates of lime and magnesia, and boiler feed water treatment in general deals with getting rid of these salts, more or less completely.

Solubility Of Mineral Salts In Water

Compound	ppm as CaCO$_3$	
	32°F (0°C)	212°F (100°C)
Calcium		
Bicarbonate	1,620	decomposes
Carbonate	15	13
Sulfate	1,290	1,250
Magnesium		
Bicarbonate	37.1	decomposes
Carbonate	101	75
Sulfate	170,000	356,000
Sodium		
Bicarbonate	38,700	decomposes
Carbonate	61,400	290,000
Chloride	225,000	243,000
Hydroxide	370,000	970,000
Sulfate	33,500	210,000

The adjacent table provides some data on the solubility of these mineral salts at various temperatures. Calcium and magnesium carbonates, are rarely present in raw make-up water, but do exist in the presence of carbon dioxide, as bicarbonates. Carbon dioxide is insoluble at 373K (212 deg. F.) and the solubility of the carbonates becomes zero.

The variation of solubility at temperatures below 212oF is dependant upon the partial pressure of the carbon dioxide. Calcium sulphate while becoming somewhat insoluble above 212°F becomes more so as the temperature increases.

Scale is also formed by the settling of mud and sediment carried in suspension in water. This may bake or be cemented into a hard scale when mixed with other scale forming ingredients.

CLASSIFICATION OF WATER HARDNESS

Hardness, which is the most widely known evidence of the presence in water of scale-forming matter, is that quality, he variation of which makes it more difficult to obtain a lather or suds from soap in one water than in another. Hardness is ordinarily classed as either temporary or permanent. Temporarily hard waters are those containing bicarbonates of lime and magnesium which may be precipitated by boiling at 212°F and which, if they contain no other scale-forming ingredients , become "soft" under such treatment.

Permanently hard waters or those containing mainly calcium sulphate which is only precipitated at the high temperatures found within the boiler, 300°F or more. The scale of hardness is an arbitrary one, and was originally based upon the number of grains of solids per gallon *(58,381 grains = one US gallon),* and waters may be classed on such a basis as follows:- 1-10 grains per gallon, soft water; 10-20 grains per gallon, moderately hard water; above 25 grains per gallon, very hard water.

Or alternatively, general guidelines for classification of waters are: 0 to 60 mg/L (milligrams per liter) as calcium carbonate is classified as soft; 61 to 120 mg/L as moderately hard; 121 to 180 mg/L as hard; and more than 180 mg/L as very hard, and hard water results in the formation of scale on the waterside of boiler tubing.

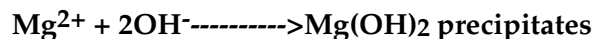| CLASSIFICATION	CARBONATE HARDNESS	NON CARBONATE HARDNESS
Calcium Hardness	Calcium Bicarbonate Ca(HCO$_3$)$_2$ Calcium Carbonate CaCO$_3$	Calcium Sulphate CaSO$_4$ Calcium Chloride CaCl$_2$
Magnesium Hardness	Magnesium Bicarbonate Mg(HCO$_3$)$_2$ Magnesium Carbonate MgCO$_3$	Magnesium Sulphate MgSO$_4$ Magnesium Chloride MgCl$_2$

Water softening is generally accomplished by chemical precipitation methods as described below, where the scale forming cations Ca^{2+} and Mg^{2+} are precipitated out of water by binding with anions

CO_3^{2-} and OH^-. to produce less soluble compounds such as $CaCO_3$, $MgCO_3$, and $Mg(OH)_2$. thereby eliminating most of these harmful scale forming compounds.

Lime Process- The lime process is used for waters containing bicarbonates of lime and magnesia. Slaked lime in solution, as lime water, is the reagent used. This combines with the carbonic acid which is present, either free, or as bicarbonates, to form an insoluble carbonate of lime. The soluble bicarbonates of lime and magnesia, losing their carbonic acid, thereby become insoluble, and precipitate. The bicarbonate hardness is eliminated:

$$Ca^{2+}$$

$$HCO_3^- + OH^- ----> H_2O + CO_3^{2-} ------------> CaCO_3 \text{ precipitates}$$
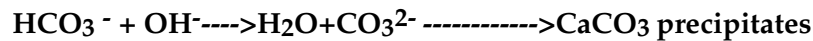
Magnesium hardness is reduced:

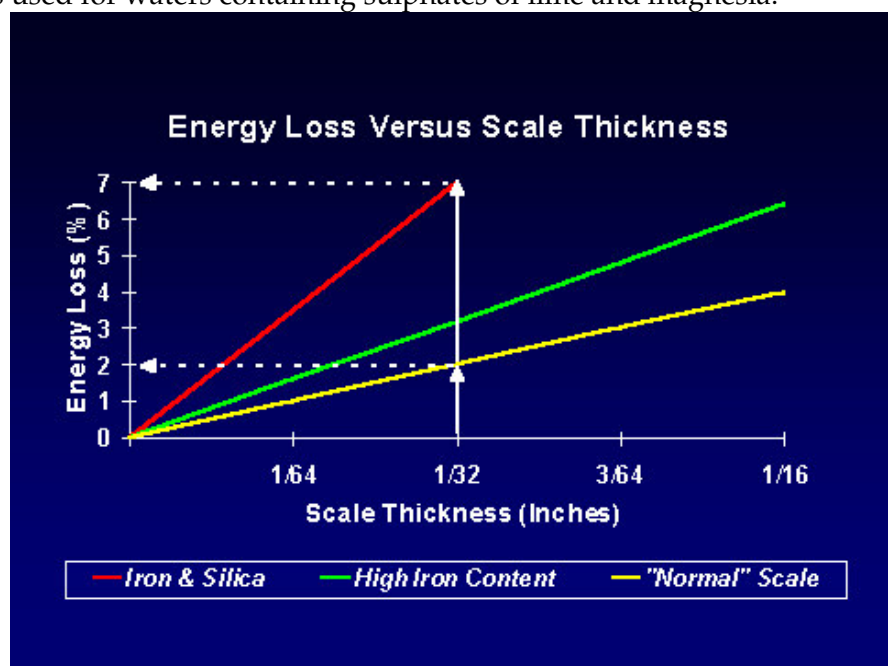$$Mg^{2+} + 2OH^- ----------> Mg(OH)_2 \text{ precipitates}$$

Soda Process- The soda process is used for waters containing sulphates of lime and magnesia. Carbonate of soda, and hydrate of soda (caustic soda) are used either alone, or together as reagents. Carbonate of soda added to the make up water, decomposes the sulphates to form insoluble carbonates of lime or magnesium, which precipitate, the neutral soda remaining in solution. If free carbonic acid (carbon dioxide) is present in the water, soluble bicarbonates of lime or magnesium are formed. When heated (deaerator) the carbon dioxide will be driven off and insoluble carbonates will be formed. Caustic soda, when used in this process, absorbs the free carbonic acid and converts the bicarbonates of lime and magnesia into insoluble the carbonates, at the same time forming either sodium carbonate or bicarbonate, according to the amount present, which in turn decomposes the sulphates present, into either carbonates or bicarbonates.

Energy Loss Versus Scale Thickness

Lime & Soda Process- This process, which is a combination of the first two, is the most commonly used treatment process, is the most widely used method in boiler water purification, and is used where sulphates of lime and magnesia are present in the water, with such a quantity of carbonic acid or bicarbonates, as to impair the action of the soda. Sufficient soda is used to break down the sulphates of lime and magnesia, and sufficient lime is added in order to absorb the carbonic acid not eliminated in the soda reaction.

$$CaCl_2 + Na_2CO_3 ----> CaCO_3 \text{ precipitates} + 2NaCl$$

$$MgSO_4 + Na_2CO_3 ----> MgCO_3 \text{ precipitates} + Na_2SO_4$$

Zeolite Process- Zeolite is a hydrated sodium aluminum silicate, and when water, containing calcium or magnesium, is passed through a bed of this material, an exchange takes place whereby the sodium of the zeolite goes into solution, and calcium and magnesium are removed. By regenerating with common industrial salt, the sodium is replaced in the zeolite. Whenever waters containing elevated

amounts of calcium or magnesium carbonate are treated using the zeolite method, an equivalent amount of sodium carbonate, or bicarbonate is carried to the boiler in the feed water. When concentrated in the boiler, this may cause priming, and in severe cases, embrittlement of the boiler plates.

Lime Zeolite Process- This employs the principles of the first, and fourth process just described. By treating with lime the carbonates are removed, and then the zeolite process is used to remove the permanent hardness. Priming dangers are significantly reduced, and the embrittlement issue is completely eliminated.

"DO IT YOURSELF" WATER TESTING

I want to say at the outset of this section, that the procedures described below are not a substitute for suitable water treatment contractor, and in depth analysis of boiler waters. However, in developing countries such as the Philippines, and elsewhere, budgetary considerations, and locations, may preclude such sophisticated analyses. However, there are simple chemical tests on boiler waters that can be undertaken by plant quality assurance, and engineering personnel, in order to ensure the correct operation of steam utilities and systems. These tests will cost less than $5 USD in materials used. I reiterate once more, that these simple tests should not be used as a substitute for the services and analyses of a professional water treatment company, if such services are readily available. If they are not, or they are beyond your means, then these simple tests will provide you with an excellent and reliable methodology for testing your boiler waters.

From a historical point of view, these tests were standard operating procedure for boiler installations from about 1900-1955, until more modern instrumentation became available. In fact the procedures detailed below were recommended by the BABCOCK AND WILCOX Company in their 1923 36th edition of "Steam Its Generation And Use" handbook , of which I am a proud owner.

My copy was given to me by my grandfather in 1965, during my fist year at polytechnic college.

So feel confident about the origin and pedigree of these simple test procedures:

Some important rules of thumb:

- The causticity should be about 2-3 times the hardness.

- The alkalinity should be about 1.5-2 times the causticity.

Summary of Principal Chemical Tests

Testing For Water Hardness
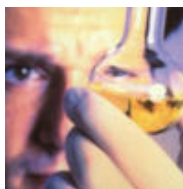
This can be accomplished with a simple soap solution, using the methodology described, and referring to the table below. You can prepare a simple inexpensive soap solution in the following manner:- Make soap solution by dissolving 1 g of shavings of plain (castile) laundry soap in 100 ml of methylated spirits.

Take a 50cc sample of the boiler make-up water to be tested. Let the sample stand in your laboratory until it has reached the ambient temperature. Add 0.1cc of the soap solution to the water sample, and shake the whole violently. Keep on adding the soap solution in 0.1cc increments, and shaking, until enough of the soap solution has been added to make a permanent foam or lather. The soap bubbles must not disappear after the shaking has stopped. Then use the table below to determine the total hardness in parts per million of CaCO3. (Calcium Carbonate).

TOTAL HARDNESS IN PPM OF CaCO$_3$ for 0.1cc OF SOAP SOLUTION WHEN A 50cc SAMPLE IS TITRATED

Soap Solution Cubic Centimeters	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.0	*	*	*	*	*	*	*	0.0	1.6	3.2
1.0	4.8	6.3	7.9	9.5	11.1	12.7	14.3	15.6	16.9	18.2
2.0	19.5	20.8	22.1	23.4	24.7	26.0	27.3	28.6	29.9	31.2
3.0	32.5	33.8	35.1	36.4	37.7	38.0	40.3	41.6	42.9	44.3
4.0	45.7	47.1	48.6	50.0	51.4	52.9	54.3	55.7	57.1	58.6
5.0	60.0	61.4	62.9	64.3	65.7	67.1	68.6	70.0	71.4	72.9
6.0	74.3	75.7	77.1	78.6	80.0	81.4	82.9	84.3	85.7	87.1
7.0	88.6	90.0	91.4	92.9	94.3	95.7	97.1	98.6	100.0	101.5

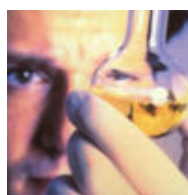| SOFT (0-60 ppm CACO$_3$)   MODERATELY HARD (61-120 ppm CACO$_3$) |
|---|

Testing For Alkalinity
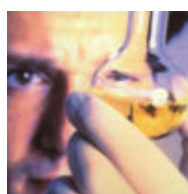
Take a 100cc sample of the boiler make-up water, let it stand in your laboratory until it has reached the ambient temperature. Add to the sample just enough methylorange to color it. Then add a 0.1cc normal sulfuric acid drop by drop, until the mixture is on the point of turning permanently red. As you start to add the acid, the red color will show quickly when the mixture is shook, and will then disappear slowly. The red color will disappear more slowly as the critical point is reached. Multiply the number of cubic centimeters (cc) of acid used by 50 equals the parts per million alkalinity as calcium carbonate.

Testing For Causticity

Take a 100cc sample of the boiler make-up water, let it stand in your laboratory until it has reached the ambient temperature. Add one drop of phenolphthalein dissolved in alcohol to give the water a pinkish color. Add the standard sulfuric acid solution, drop by drop, shaking after each addition, until the color disappears. Multiplying the cubic centimeters (cc) of acid used by 50, will equal the parts per million of causticity, as calcium carbonate.

Testing For Excess Lime

Excessive lime content of the boiler make-up water (over-treatment) can be determined by a simple go-no go test using Nitrate of Silver. If there is an excessive use of lime used during treatment, a sample (typically 50cc) will become brown by the addition of a small quantity of silver nitrate, otherwise, a milky solution will be formed. If too little lime is used, the causticity will be too low, the hardness and alkalinity too high, and scale will result. If to much lime is used, the causticity will be too high.

The Financial Impact Of Testing & Treating Your Own Boiler Waters

If your company employs chemical engineers, then there is no reason why you should not consider testing and treating your own boiler waters. Most water treatment companies will not sell their own branded chemicals without a support and analysis service, which is undertaken by their chemical engineer, or suitably trained company employee. You should understand that the services provided by water treatment contractors vary greatly from company to company, and from representative to representative. Another source of potential conflict arises when the water treatment contractor tries to sell their own chemical formulation in excessive amounts, which results in ballooning repair and maintenance budgets. Typically, chemical products that include service in the contract price,

can cost 5-20 times the price of generic chemicals.

In closing out this page I would offer the following advise:

- If your company does not employ chemical engineers, and has the financial capacity, then contract your boiler water treatment to a specialist company.
- If your company employs chemical engineers, then test and treat your own boiler waters.
- If your company does not have the financial capacity, and no chemical engineer: Send your boiler operators on a government sponsored training course. Use simple yet appropriate testing techniques, as described, and purchase generic treatment chemicals.

END

(Page Last Updated 01/05/03)

Note* This page is dedicated to my grandfather Mr. Cecil White 1885-1970

END

We Welcome Your Feedback: CLICK On The Image