

RX Marine International



Boiler Water - Problems & Solutions

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Course Content

The quality of water is important to avoid damage to the boiler. The makeup water depending on its source may contain large amount of impurities. This, if not treated shall result in fouling of boiler heat transfer surfaces and shall increase the fuel consumption. Makeup water also contains considerable amounts of dissolved oxygen which is a prime cause of corrosion. The high heat intensity of the evaporation accelerates the oxidation, scaling and corrosion process. The high heat intensity of the evaporation accelerates the oxidation, scaling and corrosion process. The pitting corrosion leads to boiler tube failures and might impurities and the dissolved oxygen loading.

A successful water treatment approach requires a total system approach to:

- prepare the water before it goes to the boiler.
- Maximize the potential of condensate.
- Provide internal boiler protection.
- Maintain clean internal boiler surfaces.
- Avoid problems and shutdowns.
- Monitor and control treatment levels.

By definition, the following terms are summarized for the boiler water systems:

1) Makeup Water - The raw water, softened water, or demineralized water required for steam generation.

2) Condensate water - when steam transfers its heat to the process, heat exchanger, or heating coil, it reverts to liquid phase called condensate. condensate water is generally very pure and when returned back to the boiler for production into steam again, does not require additional treatment chemicals. it is one of the most attractive methods of improving the boiler water quality and steam plant's energy efficiency.

3) Blowdown water - The part of water that is purposely drained to limit the level of impurities to an acceptable level. makeup water is added to compensate for the blowdown loss.

4) Feedwater - Feedwater is the aggregate of the total of condensate return and boiler makeup water that is fed to the boiler to make new steam. $\text{feed water (FW)} = \text{makeup water (MW)} + \text{Return condensate (RC)}$.

In a heavy use industrial steam boiler, the water could be completely replaced as often as once each hour. obviously at higher turnover, the boiler would quickly have scale and/or tube failures from the water impurities that would reduce and ultimately prevent water circulation and heat transfer, which shall destroy the boiler.

The higher the operating pressure of the boiler, the more critical the removal of foreign items from the feedwater becomes. Large utility boilers operating at 3,000 psig + 30y actually use distilled water for ultimate purity. As a rule, the following need to be noted:

- 1) The constituents of concern in steam cycle water are constituents that cause corrosion or fouling not only to the boiler heat transfer surfaces but also of downstream equipment such as steam turbines and process heat exchangers.
- 2) The constituents of concern for heat transfer surface corrosion include total dissolved solids [DS], free caustic, acids, dissolved oxygen and carbon dioxide.
- 3) The constituents of concern for heat transfer surface fouling include iron and copper.
- 4) The constituents of concern to major downstream equipment such as steam turbines include cation conductivity, silica, sodium, chloride, sulfate, and pH.

This American society of Mechanical Engineers (ASME) has provided guidelines for water quality. The table below reflects the maximum allowable water impurities recommended by ASME which truly reflects safe and reliable operation parameters.

Course Content

Drum Pressure, psig	Iron, ppm	Copper, ppm	Total hardness, ppm CaCO ₃	Silica, ppm SiO ₂	Total alkalinity*, ppm CaCO ₃	Specific conductance, micromhos/cm
0 to 300	0.100	0.050	0.300	150	700	7000
301 to 450	0.050	0.025	0.300	90	600	6000
451 to 600	0.030	0.020	0.200	40	500	5000
601 to 750	0.025	0.020	0.200	30	400	4000
751 to 900	0.020	0.015	0.100	20	300	3000
901 to 1000	0.020	0.015	0.050	8	200	2000

The table puts an accurate analysis of a composite feedwater sample to determine the concentration limit of the boiler water. The term 'Cycles of concentration' refers to the accumulation of impurities in the boiler water. If the boiler water contains ten times the level of impurities in the makeup water, it is said to have ten cycles of concentration. The application of the table above is as follows:

- 1) If the feedwater sample for a packaged water tube boiler operated at 100 psig shows a total alkalinity (as calcium carbonate) of 70 ppm and the maximum allowed is 700 ppm; therefore, the concentration limit is 10.
- 2) If the analyzed sample for silica (as silicon-di-oxide) indicates 4 ppm and the maximum allowed is 150 ppm, therefore, the concentration limit is 37'.
- 3) If the analyzed sample for total dissolved solids tests 390 micromhos and the maximum allowed is 7000 micromhos, therefore the concentration limit is 18'.

The requisite water quality for boiler feedwater shall be achieved through proper external treatment and proper internal treatment.

External Treatment:

External treatment, as the term is applied to water prepared for use as boiler feed water, usually refers to the chemical and mechanical treatment of the water source. The goal is to improve the quality of this source prior to its use as boiler feed water, external to the operating boiler itself. Such external treatment normally includes, clarification, filtration, softening, de-alkalization, de mineralization' Dearation' etc - Any or all of these approaches can be used in feedwater or boiler water preparation.

Internal Treatment:

Even after the best and most appropriate external treatment of the water source, boiler feed water (including return condensate) still contains impurities that could adversely affect boiler operation. internal boiler water treatment usually in form of chemical dosage/ injection is then applied to minimize the potential problems and to avoid any catastrophic failure, regardless of external treatment malfunction.

PART 1 PROBLEMS OF WATER

All raw water used for boiler makeup, irrespective of its source contains number of impurities. Water as it passes over the ground picks up some of the limestone and other elements of nature which dissolve and remain. The common impurities of water are summarized below:

Name	Description (Qualitative)
Turbidity	Finely suspended matter, which does not settle. Impart a muddy or cloudy appearance to water.
Suspended Solids	Color in natural waters is generally due to organics from decayed vegetation and organic wastes, causing water to vary from colorless to deep brown.
Color	These are substances that exist in water as suspended particles. They are usually mineral, or organic in origin. Un-dissolved matter causes turbidity and can plug lines' deposit in heat exchange equipment boilers etc. These substances are not generally a problem as they can be filtered out
Dissolved Solids	These are substances that will dissolve in water. the principal ones are the carbonates and sulphates of calcium and other dissolved solids, which are non - scale forming. The total amount of dissolved matter excluding dissolved gasses is determined by evaporation.
Total Solids	The sum of suspended solids and dissolved solids is determined
Hardness	calcium and magnesium salts which are the chief source of scale
Alkalinity	Bicarbonate (HCO_3), carbonate (CO_3) and hydrate (OH) measured by titration. Alkalinity can convert to CO_2 in steam and cause corrosion
Free Mineral Acidity	H_2SO_4 , HCl etc

Name	Description (Qualitative)
Dissolved Gases	Oxygen and carbon dioxide can be readily dissolved by water. These gases are aggressive instigators of corrosion.
Cations	Positively charged ions such as calcium, Ca ⁺⁺ , magnesium Mg ⁺⁺ , sodium Na ⁺ and potassium K ⁺
Anions	Negatively charged ions such as alkalinity, sulphate (Soa), chloride and nitrate (N03)
Silica	Normally exists in water as an anion (HSiO ₂) ⁻ or as a colloidal suspension.
Iron and Manganese	Can exist in water as a dissolved cation but readily precipitates and cause discoloration and fouling.
Oil and Grease	Can exist in water as an emulsion causing foaming and fouling.

In context to boiler water, the first noticeable observation is hardness, which is composed primarily of calcium (ca⁺⁺) and magnesium (mg⁺⁺) minerals. The hardness is primarily responsible for scale formation. The other elements and their effect to boiler surfaces are listed below:

Name	Common Name	Effect
Calcium carbonate, CaCO ₃	Chalk, limestone	Soft scale
Calcium bicarbonate, CaHCO ₃	--	Soft scale, Co2
Calcium sulphate, CaSO ₄	Gypsum, plaster of paris	Hard Scale
Calcium chloride CaCl ₂	—	Corrosion
Magnesium carbonate, MgCO ₃	Magnesite	Soft Scale
Magnesium bicarbonate, MgHCO ₃	—	Scale, Corrosion
Magnesium sulphate, MgSO ₄	Epsom Salt	Corrosion
Sodium Chloride, NaCl	Epsom Salt	Electrolysis

Name	Common Name	Effect
Sodium carbonate, Na_2CO_3	Washing Soda	Alkalinity
Sodium bicarbonate, NaHCO_3	Baking Soda	Priming, Foaming
Sodium hydroxide, NaOH	Caustic Soda	Alkalinity, embrittlement
Sodium sulphate, Na_2SO_4	Glauber salts	Alkalinity
Silicon dioxide, SiO_2	Silica	Hard Scale

Before we proceed further, it is necessary to establish a definition of water quality parameters:

Conductivity: A measure of water's ability to conduct electricity in cooling water. It indicates the amount of dissolved minerals in water. Conductivity is measured in micro-mhos and can vary from a few for distilled water to over 10000 for saline water.

pH: pH is the measure of the degree of acidity or basicity of solution. The pH scale ranges from 0 to 14, with zero being the most acidic and 14 the most basic or alkaline. Control of pH is critical for the majority of boiler water treatment programs.

Key indicators are:

- A change of one PH value represents a change of 10 times in relative acidity or alkalinity. for example, a PH of 4 is ten times more acidic than a pH of 5.
- Acids and alkalis have the effect of increasing the conductivity of water above that of a neutral sample. for example, a sample of water with a PH value of 12 will have a higher conductivity than a sample that has a PH value of 7.
- In general, when Ph is below recommended ranges, the chances for corrosion increase and when PH is above recommended ranges, the chances for scale formation increase.
- According to ASME guidelines, the boiler water's level of PH must be maintained above 9.5 to ensure that the proper chemical reaction occurs between the calcium and magnesium ions and the phosphate molecules.

Alkalinity: Alkalinity is a measure of the bicarbonate (HCO_3), carbonate (CO_3), and hydroxyl (OH) ions in water. it is possible for these ions to exist simultaneously; though, only the bicarbonate and carbonate ions are found in natural water supplies.

key indicators are:

- In boiler feed water, two forms of alkalinity are the carbonate (CO_3) alkalinity and bicarbonate (HCO_3) alkalinity. Bicarbonate alkalinity is by far the most common.
- M alkalinity, or total alkalinity, is defined as the sum of carbonate, bicarbonate, and hydroxide.
- Palkalinity, or phenophthalein, is defined as one half of the carbonate alkalinity plus all of the hydroxide alkalinity.
- Carbonate and bicarbonate alkalinities can combine with calcium and magnesium hardness to form scale in boiler water systems.
- Alkalinity and pH are related because increase in pH indicates increases in alkalinity and vice versa.
- When water with carbonate or bicarbonate alkalinity is heated, the alkalinity is broken down to carbon dioxide. The CO_2 released, combines with the water to give carbonic acid, which can cause corrosion of the boiler internals. The corrosion products react further with alkalinity and the deposits can build up in the same manner as calcium carbonate scale.

Hardness: water is referred to as being either 'hard or soft'. hard water contains scale - forming impurities while soft water contains little or none.

Key indicators are:

- Hardness is composed primarily of calcium (Ca^{++}) and magnesium (Mg^{++}) minerals. These are primarily responsible for scale formation. The sum of these two is the total hardness.
- The total hardness is then broken down into two categories.
 - **carbonate or temporary hardness:** Calcium and magnesium bicarbonates are responsible for alkaline hardness. The salts dissolve in water to form an alkaline solution. when heat is applied, they decompose to release carbon
 - **Non- Carbonate or permanent Hardness:** This is also due to the presence of the salts of calcium and magnesium but in the form of sulphates and chlorides. These precipitate out of solution, due to their reduced solubility as the temperature rises, and form hard scale, which is difficult to remove.
- Hardness, particularly the temporary hardness is the most common and is responsible for the deposition of calcium carbonate scale.
- If the water is alkaline, a proportion of hardness, equal in magnitude to the total alkalinity (expressed as CaCO_3) is considered as alkaline hardness, and the remainder as non- alkaline hardness.
- The presence of silica in boiler water can also lead to hard scale, which can react with calcium and magnesium salts to form silicates which can severely inhibit heat transfer across the fire tubes and cause them to overheat.
- Hardness is measured in grains or parts per million, with one grain of hardness being 17.1 ppm of these elements.
- The hardness is removed from the water by a process known as positive ion exchanged for the calcium and magnesium ions, as the water passes through the softener tank.

The other important parameters are:

- 1) **Total Suspended solids:** The measure of particulate matter suspended in a sample of water or wastewater. After filtering a sample of a known volume, the filter is dried and weighed to determine the residue retained. The amount of suspended solids measured in mg/l
- 2) **Total Dissolved solids (TDS):** This represents all the dissolved constituents for e.g. Ca , Cl , and Na etc. it is measured in Mg/l . the terms TDS and conductivity of water are interrelated.
- 3) **Total Cations:** Cations are metallic parts and carry positive charges - calcium , sodium, magnesium are attracted to the cathode.
- 4) **Total Anions:** Anions are non- metallic and carry negative charges - bicarbonates, carbonate, chloride, sulphate, are attracted to the anode.
- 5) **BOD:** Signify Biological Oxygen demand and is measured in mg/l .
- 6) **COD:** chemical Oxygen Demand and is measured in mg/l .
- 7) **TOC:** Total Organic carbon and is measured in Mg/l
- 8) Total silica that is measured in Mg/l of SiO_2
- 9) **Turbidity:** signify suspended matter in water or wastewater that scatters or otherwise interferes with the passage of light through the water.

WATER RELATED PROBLEMS

The chemistry of water has a direct impact on the two main problems of boiler water system;

- 1) scale
- 2) corrosion

Both of these arise from different group of contaminants. The former is due to deposition of Ca and Mg salts at high temperatures into products like carbonate, hydroxide, sulphate and silicates. The products of corrosion for example, silt and sludge may also add to scale formation.

The corrosion springs from dissolved gases like O₂ in feed water and CO₂ originating from the decomposition of carbonates and bicarbonates at high boiler temperatures.

SCALE DEPOSITS:

Water impurities such as calcium, magnesium and silica, commonly found in most water supplies precipitate at high temperature and form a dense coating of material on the waterside of the boiler tubes. This layer of coating is technically known as 'scale'. The character of these scales may vary from very dense to porous, from loosely held to tenaciously bonded to the surface.

The key points to note here are:

- 1) Scale typically has a thermal conductivity of an order of magnitude less than the corresponding value for bare steel. Even these layers of scale serve as an effective insulator and retard heat transfer.
- 2) Scale in addition to its high insulating value; progressively narrows pipe internal diameters, roughens tube surfaces and impedes proper flow.
- 3) Scale causes the tubes' metal temperature to rise, which increases the flue gas temperature. In extreme cases, the tubes fail from overheating.
- 4) Scale causes fuel wastage typically up to 2% for water-tube boilers and up to 5% in fire-tube boilers.

Principle Factors Responsible for Scale Formation

- 1) Calcium, magnesium and silica concentration.
- 2) Alkalinity of water (or pH > 7).
- 3) High operating temperatures.
- 4) High concentration of solids (TDS).
- 5) Insufficient blow down.
- 6) Low condensate recirculation.

Ca & Mg hardness isn't the only cause. Other impurities such as iron, silica, copper, oil, etc. are often found in samples of boiler scale. In fact, it is rare to find scale which isn't the result of several of these impurities.

How do these factors increase the amount of scaling?

As any of the above factors changes, scaling tendencies also change.

Higher the level of scale-forming salts, the greater shall be the chances of scale formation. Hardness levels are primarily associated with the tendencies of feed water to be scale-forming or not.

Most salts become more soluble as temperature increases. However, some salts, such as calcium carbonate, become less soluble as temperature increases. Therefore they often cause deposits at higher temperatures.

A change in pH or alkalinity can greatly affect scale formation. As alkalinity increases, salts such as calcium carbonate decreases in solubility and therefore results in deposits at high alkalinity.

Some materials, such as silica (SiO_2) are less soluble at lower alkalinities.

How can scale formation be controlled ?

Any scale in a boiler is undesirable. The best way to deal with scale is not to let it form in first place. scale formation is prevented by :

- 1) External pretreatment of boiler make-up water (using water softeners, dealkalizers, and reverse osmosis) to remove hardness/scale-forming minerals before they enter the boiler system.
- 2) Internal treatment using chemical formulation into the boiler feed water for instance phosphate treatment to keep the common scale forming materials in dissolved form.
- 3) Adopting proper boiler blowdown practices to limit the concentration of scale forming materials by controlling cycles of concentration. A part of water is purposely drained off (blow down) to prevent minerals built up. A cycle of concentration is the ratio of the make-up rate to the blow down rate.
- 4) The boiler feed water is sum of condensate return + makeup water. The condensate water produced as a result of condensation of evaporated steam is very pure and free of hardness causing salts. Thus higher the make up water, the higher shall be the impurities and higher will be scale forming tendencies.

How does the internal chemical treatment work ?

There are two primary methods used to control hardness in internal boiler treatment problems: the carbonate cycle and the phosphate cycle. In general the carbonate cycle is recommended for system with operating pressures below 125 psig. The phosphate cycle is recommended for system with operating pressure above 125 psig.

The carbonate cycle is based upon the principle of precipitating the hardness in the form of carbonate. This reaction proceeds in the following manner: $(\text{Ca}^{++}) + (2\text{HCO}_3^-) + \text{heat/pressure} = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

Once the hardness precipitate is formed, is conditioned through the use of synthetic or natural polymers. In a physical reaction, the calcium carbonate molecule is attach to the polymer molecule and dropped to the bottom of the boiler as fluid sludge. As the polymer molecules begin to accumulate at the bottom of the boiler, they are removed from the boiler through bottom blowdown.

The phosphate cycle is based upon the principle of precipitating the calcium and magnesium hardness with phosphate. Once the hardness/phosphate precipitate is formed, it also is conditioned as sludge through the use of synthetic or natural polymers. In this physical reaction, many calcium phosphate molecules attach to one polymer molecule and drop as fluid sludge to the bottom of the boiler, where they can be blow down. According to ASME guidelines, the boilers waters level of pH must be maintained above 9.5 to ensure that the proper chemical reaction occurs between the calcium and magnesium ions and the phosphate molecules.

Should unexpected hardness result, a phosphate residual should be maintained. However, this is major disadvantage to using a phosphate to precipitate hardness. Magnesium phosphate forms a very sticky sludge, and frequently the sludge drops onto the heat transfer surfaces and forms deposits.

How does the scale conditioning work ?

Scale conditioners modify the crystal structure of scale, creating a bulky transportable sludge instead of hard deposit.

When hardness is controlled through carbonate and phosphate programs, the resulting sludge must be conditioned into a fluid substance ease in bottom blowdown. sludge conditioners are generally very long synthetic or natural chains of polymeric molecules. The sludge conditioner physically bonds with the calcium carbonate or phosphate formed in the boiler to prevent the formation of precipitated scale on the heat transfer surfaces.

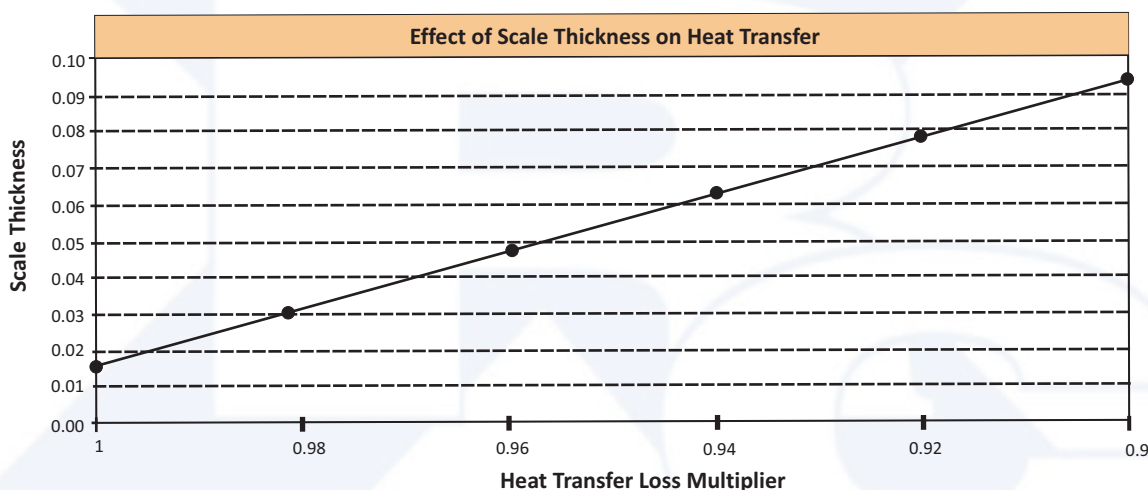
Several of the most popular internal boiler sludge conditioners are sodium polymethacrylate and sulfonated copolymers.

It is important to remember that an effective bottom blowdown schedule must be maintained to ensure that the conditioned sludge is removed from the boiler.

How does the scale deposits Energy Consumption ?

As a rule of thumb, one millimeter of scale build-up can increase fuel consumption by two percent.

The figures below bring out the importance of the scales and its influence on energy conservation.



Energy Loss due to Scale Deposits			
Scale Thickness, inches	Fuel Loss, % of Total Use		
	"Normal"	Scale Type High Iron	Iron Plus Silica
1/64	1.0	1.6	3.5
1/32	2.0	3.1	7.0
3/64	3.0	4.7	—
1/16	3.9	6.2	—

It is intuitively obviously that the presence of even the low thickness scale can cause considerable reduce that transfer rates across sensitive boiler surface, amounting to large fuel rate consumption for equivalent boiler rating and capacity.

What symptoms indicates likelihood of scale ?

1) Flue Gas Temperature:

An indirect indicator of scale or deposit formation is flue gas temperature. An upward trend in flue gas temperatures over weeks or months usually indicate that a deposit has built up on either the fire side or waterside of boiler heat-exchange surface. The boiler should be inspected promptly.

2) Visual Inspection:

Visually inspect boiler tubes when the unit is shut down for maintenance. Scale removal can be achieved by mechanic means or acid cleaning. If scale is present, consult with your local water treatment specialist and consider modifying your feed water treatment or chemical additives schedule.

How to prevent scale formation from happening ?

The first and foremost aspect of stopping scale formation is to have a good idea of the makeup water that is feeding your system. If you aren't sure, have a certified laboratory complete a full analysis on the water, so you can make an informed decision on what exactly the potential problems you may encounter.

After determining these specific aspects of your makeup water, one can consult a water treatment expert who can guide you through a program that fits your situation. A complete program will generally include sludge build up, pH levels, oxygen removal, condensate treatment and alkalinity levels.

Normally pre-softening the water before feeding it to the boiler is the first step in eliminating scale formations. Even when the makeup is soft, there is still a need for chemical scale inhibitors inside the boiler. With proper treatment, the problems of lost efficiency, tube damage and lost production can be avoided or greatly reduced. Proper treatment requires the right balance of chemical treatment and control.

A cursory overview of the various possibilities is provided later in this course.

CORROSION:

What causes corrosion in boilers ?

The most common source of corrosion in boiler systems is dissolved gases: oxygen, carbon dioxide and ammonia. Of these, oxygen is the most aggressive. The importance of eliminating oxygen as a source of pitting and iron deposition cannot be over-emphasized. Even small concentrations of this gas can cause serious corrosion problems.

Makeup water introduced appreciable amounts of oxygen into the system. Oxygen can also enter the feed water system from the condensate return system. possible return line sources are direct air-leakage on the suction side of pumps, system under vacuum, the breathing action of closed condensate receiving tanks, open condensate receiving tanks and leakage of non-deaerated water used for condensate pump seal and/or quench water. With all of these sources, good housekeeping is an essential part of the preventive program.

What types of corrosion exists in boiler water systems ?

The most common type of boiler corrosion is localized 'Pitting attack'. The main source for pitting attack is dissolved oxygen, which causes small but deep pinpoint holes that eventually penetrate boiler tube walls and cause their failure. Only small area of the metal corrodes, but it is enough to cause major disruptions of boiler systems. The degree of oxygen attack depends on the concentration of dissolved oxygen, the pH and the temperature of the water.

The other types is the general attack where the corrosion is uniformly distributed over the metal surface throughout the boiler system network. The considerable amount of iron oxide produced due to general corrosion contributed to fouling problems.

What water characteristics affect corrosion ?

- 1) Oxygen and other dissolved gasses.
- 2) Dissolved or suspended solids.
- 3) Acidity (or $\text{pH} < 7$).
- 4) Velocity.
- 5) Temperature.

In general corrosion in boilers can always be traced to one or both of the following problems.

First, the dissolved oxygen entering the system via the feed-water or can infiltrate the boiler system at virtually any point. Oxygen dissolved in water is essential for the cathodic reaction to take place.

Second common cause of corrosion in boiler system is low pH within the boiler. This reduced pH may result from CO_2 infiltration or form contamination by other chemicals.

How do dissolved or suspended solids affect corrosion ?

Dissolved solids can affect the corrosion reaction by increasing the electrical conductivity and more is the likelihood of corrosion. Dissolved chlorides and sulphates are particularly corrosive.

How does alkalinity or acidity corrosion ?

Acidic and slightly alkaline water can dissolve metal and the protective oxide film on metal surfaces. More alkaline water favors the formation of the protective oxide layer. To prevent corrosion the boiler water needs to be somewhat alkaline and not acidic.

Standard practices call for maintaining pH 10.5 - 11.5 for shell boilers @ 150 psig. pH of 9 could be used in higher pressure boilers. Variations from the levels that are considered optimum for maintenance of the magnetite layer can cause general corrosion either due to acidic or caustic attack.

- **Acidic Attack:** If boiler water pH has dropped significantly below 8.5, a phenomenon called waterside thinning can occur. The normal manifestation of acidic attack is etching. In areas of higher flow, the surfaces are smooth. In addition, stressed area would be a principle area for attack.
- **Caustic Attack :** Caustic attack is essentially stripping of the magnetite film and typically occurs due to extremely high pH of 12.9+. caustic corrosion is often encountered in phosphate treated boilers in which deposits occur in high heat transfers areas. Typically a 1% caustic solution is used to achieve a target pH of between 9 and 11.

How alkalinity control is important in preventing corrosion ?

Alkalinity control is vital to the success of any internal boiler treatment program. Alkalinity in a boiler system protects the unit against attack and maintains the proper pH level for the necessary chemical reactions to occur. Just as importantly, alkalinity provides hydroxyl ions, which form an insoluble ferrous hydroxide film on metal.

The level of alkalinity required in a boiler system depends upon several factors. Most often, however, the level of alkalinity is related to the operating pressure of the boiler.

in situations where the calcium and magnesium hardness has been removed mechanically through the use of a sodium exchange softener, alkalinity control can be achieved without the addition of chemical alkalinity builders. A feed water analysis will show whether proper alkalinity can achieved without the use of supplemental chemicals.

How does the water velocity affect corrosion ?

High velocity water increases corrosion by transporting oxygen to the metal and carrying away the products of corrosion at a faster rate. When water velocity is low, deposition of suspended solids can establish localized corrosion cells, thereby increasing corrosion rates.

How does temperature affect corrosion ?

The influence of temperature on the corrosivity of dissolved oxygen is particularly important in closed heaters and economizers where the water temperature increases rapidly. Elevated temperature in itself does not cause corrosion but small concentration of oxygen at elevated temperature do cause severe problems. This temperature rise provides the driving force that accelerates the reaction so that even small quantities of dissolved oxygen can cause serious corrosion.

As a rule of thumb, every 25-30 F increases in temperature causes corrosion rates to double.

Which materials are susceptible to corrosion ?

Carbon steel is a commodity used metal in the construction of boiler system that is most susceptible to corrosion. Iron is carried into the boiler in various forms of chemical composition and physical state. Most of the iron found in the boiler enters as iron oxide or hydroxide. Any soluble iron in the feedwater is converted to the insoluble hydroxide when exposed to the high alkalinity & temperature in the boiler.

These iron compounds are divided roughly into two types, red iron oxide (Fe_2O_3) and black magnetic oxide (Fe_3O_4). The red oxide (hematite) is formed under oxidizing condition that exist, for example, in the condensate system or in a boiler that is out of service. The black oxides (magnetite) are formed under reducing conditions that typically exist in an operating boiler.

Other metals in general, such as copper, stainless steel, aluminum alloys also do corrode but the process is slow. However in some waters and in presence of dissolved gases, such as H_2S or NH_3 , the corrosion to these metals more severe & destructive than to mild steel.

What methods are used to remove O_2 and CO_2 to prevent corrosion ?

1) Oxygen corrosion :

The most harmful of the dissolved gases is oxygen. Even very small amounts of oxygen can cause severe damage. The amount of dissolved oxygen present in the system is dependent on the temperature of the feedwater; the lower the feedwater temperature, the larger the volume of dissolved oxygen present. The oxygen can be removed both mechanically and chemically.

The mechanical methods for controlling oxygen include deaerators and vacuum degasifiers.

Any remaining oxygen is dealt with by the addition of a chemical oxygen scavenger such as catalyzed sodium sulphite. Typically, 8 ppm of sodium sulphite is sufficient to deal with 1 ppm of dissolved oxygen.

2) Carbon dioxide corrosion:

Carbon dioxide corrosion is normally controlled by driving the CO_2 from the water in an aerator or decarbonator. Both reduce CO_2 concentration to 5-10 ppm range.

The carbon dioxide concentration in the effluent from a vacuum degasifier is typically 5 ppm. The effluent concentration may be different if the vacuum degasifier is sized for oxygen reduction rather than carbon dioxide reduction.

Chemical inhibitors in form of neutralizing amines are generally used.

What is purpose of deaerator ?

Makeup water introduce appreciable amounts of oxygen into the system. Oxygen Can also enter the feed water system from the condensate return system.

Since makeup water contains considerable amounts of dissolved oxygen, corrosion becomes a critical reliability concern, because high heat intensity at the boiler tubes accelerates the oxidation process. Therefore, feedwater to the boiler must be made oxygen free. Generally the higher the makeup water, the higher is the dissolved oxygen loading.

Deaerator is most commonly used equipment to get rid of dissolved oxygen. Very briefly, the deaeration process uses live steam and mechanical agitation to encourage dissolved oxygen to escape from the water. The liberated dissolved oxygen must be continuously removed from the deaerator, and hence, a small purge stream normally one percent of boiler capacity has been accepted industrial norm.

Simply speaking, the purpose of deaeration is :

- 1) To remove oxygen, carbon dioxide and other non-condensable gases from feed water.
- 2) To heat the incoming makeup water and return condensate to an optimum temperature for minimizing solubility of the undesirable gases and providing the highest temperature water for injection to the boiler.

Do you require additional treatment when Deaerator is installed ?

Yes. complete oxygen removal cannot be attained by mechanical deaeration alone. Equipment manufacturers state that a properly operated deaerating heater can be mechanically reduce the dissolved oxygen concentration in the feed water to 0.005 cc per liter (7 ppb) and zero free carbon dioxide. Typically, plant oxygen level vary from 3 to 50 ppb. Traces of dissolved oxygen remaining in the feed water can then be chemically removed with the oxygen scavenger, usually catalyzed sodium sulfite. It is common practice to maintain a sulfite residual of 5-10 ppm in the feedwater and, if necessary, feed sufficient caustic soda or neutralizing amine to increase the feed water pH to between 8.0 and 9.0.

How do chemical corrosion inhibitors work ?

Chemical inhibitors reduce or stop corrosion by interfering with corrosion mechanism. Inhibiting usually affect either the anode or the cathode.

Anodic corrosion inhibitors establish a protective film on the anode. Though these inhibitors can be effective, they can be dangerous, if sufficient anodic inhibitor is present, the entire corrosion potential occurs at the unprotected anode sites. This causes severe localized (or pitting) attack. Cathodic corrosion inhibitors form a protective film on the cathode. These inhibitors reduce the corrosion rate in direct proportion to the reduction of cathodic area.

General corrosion inhibitors protect by filming all metal surfaces whether anodic or cathodic.

What inhibitors are commonly used O₂ scavenging ?

Internal treatment for dissolved oxygen corrosion is normally accomplished by the addition of sodium sulfite with the oxygen. In systems equipped with a deaerator, the sulfite should be fed to the storage tank of the deaerator, the sulfite can be fed at almost any point in the feed water system, including the condensate tank.

The common chemicals other than sodium sulfite/bisulfite are :

- 1) Hydrazine
- 2) Carbohydrazide
- 3) Organic based oxygen scavenger (such as hydroquinone, diethyl hydroxide amine, or methyl ethyl ketoxime).

All the above types remove even trace amount of oxygen.

What inhibitors are commonly used for CO₂ Removal ?

Internal treatment for carbon dioxide is normally accomplished by the use of a volatile amine. "Amine" refers to any of number of chemicals derived from ammonia. There are two major groups of amines in practice, normally referred to as "neutralizing amines" or "filming amines" depending upon whether they neutralize the acid formed by carbon dioxide or form a protective film on the metal.

- 1) Filming amines do not neutralize the carbonic acid which forms in condensate system. Instead, they form a film on the metal which is non-wettable, or impervious to water. This protective film prevents the corrosive impurities from contacting the metal. By design, film formers have been developed to function best at a pH of 5.5-7.5. In addition, these amines are highly surface- active and will slough loosely adherent iron oxide and other corrosion products back to receiving points in the boiler. Care must be exercised with the feed of filming amines.
- 2) Neutralizing amines function by increasing the pH of the condensate. Normally they are fed at such a rate that the pH of the condensate is maintained slightly above 7.0. Satisfactory reduction of carbon dioxide corrosion is possible with the use of a neutralizing amine. It is necessary to supplement this type of condensate protection with an oxygen scavenger to remove dissolved oxygen.

PART II MAKEUP WATER - TREATMENT APPROACHES

The makeup water essentially raw water may be supplied from the municipal water system, well water, or other sources. Since the list of likely raw water impurities is so large and in any sample a different set may be present to varying degrees, it is obvious that no single treatment that may be offered will depend on the careful analysis of water sample.

The most common found water treatment for industrial boilers is water softener, which works on a principle of ion exchange. In the large installation, where quality of steam is prime concern, demineralizer system is commonly used.

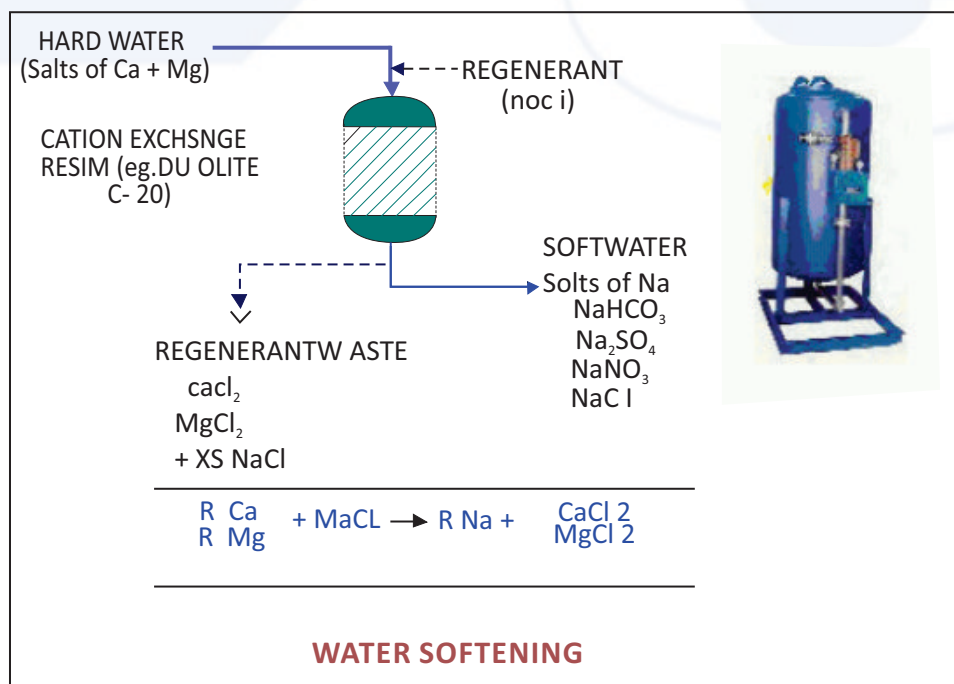
ION EXCHANGE-WATER SOFTENER:

The purpose of a water softener is to remove hardness from the boiler makeup water.

The softening media is commonly called resin or zeolite. The proper name for it is polystyrene resin. The resin has the ability to attract positive charges to itself. The reason it does so is because in its manufacture it inherits a negative charge. It is a law of nature that opposite charges attract, i.e., a negative will attract a positive and vice versa. A softener tank contains hundreds of thousands of zeolite beads. Each bead is a negative in nature and can be charged or regenerated with positive ions. In a softener, the zeolite is charged with positive ions. In a softener, the Zeolite is charged with positive, "soft" sodium ions.

As "hard" water passes through the zeolite, the calcium & magnesium ions are strongly attracted to the beds. As the "hard" ions attach to the "soft" sodium ions that are already attached to the bead, in effect the sodium (Na) is "exchanged" for the calcium & magnesium, with the Ca & Mg remaining on the zeolite beads and the Na ions taking their place in the water flowing through the softener tank. The result of this "exchange" process is soft water flowing out of the tank.

Figure below illustrates the regeneration/service cycle of a water softener and shows the various ion-exchange reactions that take place.



A softener will continue to produce soft water as long as there are sodium ions remaining on the resin to "exchange" with the calcium & magnesium ions in the hard water. When the supply of sodium ions has been depleted, the resin must be regenerated with a new supply of sodium ions.

How is regeneration process accomplished ?

The regeneration process of the resin beads is accomplished by a three step process.

- 1) **Backwash:** The flow of water through the mineral bed is reversed. The mineral bed is loosened and accumulated sediment is washed to the drain by the upward flow of the water. An automatic backwash flow controller maintains the proper flow rate to prevent the loss of resin.
- 2) **Brine Draw and Slow Rinse:** Ordinary salt has the capability to restore the exchange capacity of the mineral. A given amount of salt-brine is rinsed slowly through the mineral bed. After the salt-brine is drawn, the unit will continue to rinse slowly with water to remove all of the salt-brine from the media bed.
- 3) **Fast Rinse :** A high down flow of water repacks the mineral bed. Any trace of brine not removed in slow rinse is flushed to the drain.

The unit is then returned to service. The brine maker is refilled with fresh water to form salt brine for the next regeneration. The total regeneration times is approximately 60-90 minutes.

What factors impact the design of ion Exchange system ?

A reasonably accurate water analysis is required to design an ion exchange installation for water treatment following ions are most commonly found in water sample.

- 1) Alkaline Earth Cations : Ca^{++} or Mg^{++}
- 2) Alkaline Metal Cations : Na^+ , K^+
- 3) Total Alkalinity (ALK) : OH^- , CO_3^{--} , AND HCO_3^-
- 4) Total Salts of Strong Acids (TMA) : SO_4^{--} , Cl^- , NO_3^-

How is the water chemistry expressed?

The water chemistry in engineering parlance is described in grains per gallon and parts per million. (1 grain of hardness = ~ 17 ppm of hardness elements)

Let's say the result of the hardness test is 20 ppm. This means that for every 1 million pounds of water, there are 20 pounds of hardness salts (dissolved calcium and magnesium)

Hardness in ppm may be converted to grains per gallon by dividing the ppm reading by 17.

Example : Water hardness of 170 ppm is converted to grains per gallon.
170 divided 17=10 grains per gallon.

It is common practice to express the amount of dissolved impurities as the cations and anions. These amounts may be expressed in terms of the ions themselves or as their calcium carbonate equivalents. The later is more prevalent among engineers.

How to convert an ion concentration to CaCO_3 equivalent ?

To convert water analysis ppm as calcium carbonate, follow the steps below or refer to a standard calcium carbonate conversion table in chemical books.

- 1) Step#1 : Find the equivalents weight of ion in question and divide it by 50, which is the equivalent weight of calcium carbonate.

- 2) Step#2 : Multiple the quotient by the part per million (ppm) concentration as the ion.
- 3) Step#3 : After complete conversion to calcium carbonate equivalents, check the sum of the total anions.

Why Ion Exchange Resins are Important ?

Resin is a heart of ion - exchange system. The resins perform a function of exchanging the undesirable ions in the water to the desirable ones. There are many ion-exchange resins available today. By careful choice of the individual ion-exchange resin or in combination thereof, it is possible to design many different types of system to accomplish the same end. Any wrong selection shall have the impact on the final effluent from the system. It is strongly recommended to consult a manufacturer or an experienced water treatment design engineer for the right selection.

What are Zeolites?

Zeolites are complex silicates consisting of macromolecules of several metallic and non-metallic oxides. These are simply represented as Na_2Ze . They hold sodium ion in loose fashion and consequently when they are treated with a solution containing positive ions such as Ca & Mg, these shall be exchanged with sodium ions contained zeolite, are more effective than natural zeolite, but are less durable. These are not capable of resisting acids, and therefore cannot be used in the exchange of hydrogen ions. The suspended impurities can clog the zeolite bed thus hindering the function.

How to estimate the softener capacity?

The softener capacity is governed by the amount of resin. The amount of hardness removed by one cubic foot of cation-exchange resin is directly dependent on the amount of regenerate salt used to convert the resin to the sodium form. The capacity of softener can be sized from the formula below:

$$C = M * T * H / R$$

C = Capacity of softener in cubic feet of resin

M = Makeup water volume per hour in gallons; the volume needed to be softened (8.34 pounds per gallon)

T = Time in hours desired between regeneration cycles

H = Hardness of water in grains (17.1 ppm per grain hardness)

R = Resin Capacity per cubic foot (this is virtually always 30,000 grains)

How to estimate the chemicals required?

The amount of chemicals required for using in this method may be estimated from the following:

Calcium Hydroxide required per 1000 liters of water to be treated = $0.0007 \times (\text{CaCO}_3 \text{ in mg/liter} + \text{MgCO}_3 \text{ in Mg/Liter})$ in Kg

Sodium Carbonate required per 1000 liter of water to be treated = $0.0011 \times (\text{non-carbonate hardness in mg/liter})$

Sodium Aluminate's required per 1000 liters of water to be treated = $0.02 \times (\text{total hardness as CaCO}_3)$

This is supposed to provide the guidelines up to a maximum of 200 mg/liter hardness. In case of higher hardness levels in the form of CaCO_3 , the quantity of sodium aluminate may have to be increased by about 50% or so.

What are the limitations of softening?

Use of the sodium zeolite process on makeup water with a high alkalinity may result in excessive boiler water alkalinity and little or no reduction in blowdown. The sodium-cycle water softener removes the hardness from the water but allows the alkalinity to be carried forward.

When un-softened water is used, all hardness should be removed by precipitation within the boiler through the application of chemical. A portion of the alkalinity is also precipitated by this approach.

Little or no alkalinity is removed by zeolite softening, so alkalinity could be a limiting feedwater constituent. The alkalinities need to be treated with a process known as de-alkalization.

waters exceeding hardness above 1500 ppm require somewhat different arrangements of equipment and techniques of regeneration.

what configurations can you buy your softeners?

water softeners come as single mineral tank units (simplex), double mineral tank units (duplex) and multiple mineral tank units. since regeneration cycles can take approximately one hour simplex units are used only when this interruption can be tolerated. to avoid interruption duplex units are used so that the regeneration of one unit can be accomplished while the second unit is on line. Triplex or other multiplex units usually are the result of need for increased capacity and units can be added to keep soft water available. The reliability of new electronic metering / controls for regeneration has allowed users to depend on smaller units with more frequent regeneration.

summarizing:

Softening process consists of passing hard water through a column of cation-exchange resin in the sodium form. The sodium on the resin replaces the objectionable calcium and magnesium ions. with sodium base-exchange softening, there is no reduction in the total dissolved solids level (TDS in parts per million or ppm) and no change in the pH or alkalinity. Softeners are relatively cheap to operate and can produce treated water reliably for many years. They can be used successfully even in alkaline (Temporary) hardness areas provided that at least 50% of condensate is returned. where there is little or no condensate return, a more sophisticated type of ion exchange is preferable.

DEALKALIZATION BY ION EXCHANGE:

The disadvantage of base-exchange softening is that there is no reduction in the TDS and alkalinity. This may be overcome by the prior removal of the alkalinity and this is usually achieved through the use of a dealkalizer.

There are several types of dealkalizer but the most common varieties are split-stream dealkalization and chloride dealkalization.

split-stream dealkalization: Split-stream dealkalization employs two cation exchange units operated in parallel, one is conventional sodium zeolite softener regenerated with salt, and the other contains the same type of resin but is regenerated with acid. A portion of makeup water passes through the sodium zeolite to remove hardness by exchanging calcium and magnesium for sodium, and the remainder goes through acidified zeolite for removal of hardness and alkalinity. The hydrogen-cycle cation unit removes the hardness from the water and also creates some free mineral acidity.

These two flows are then blended and passed through aerator or de-carbonator. when these two flows are blended, the free mineral acidity from the hydrogen-cycle cation unit reacts with the alkalinity from the water softener to produce carbon dioxide and water. The CO₂ can be eliminated by aeration or degasification.

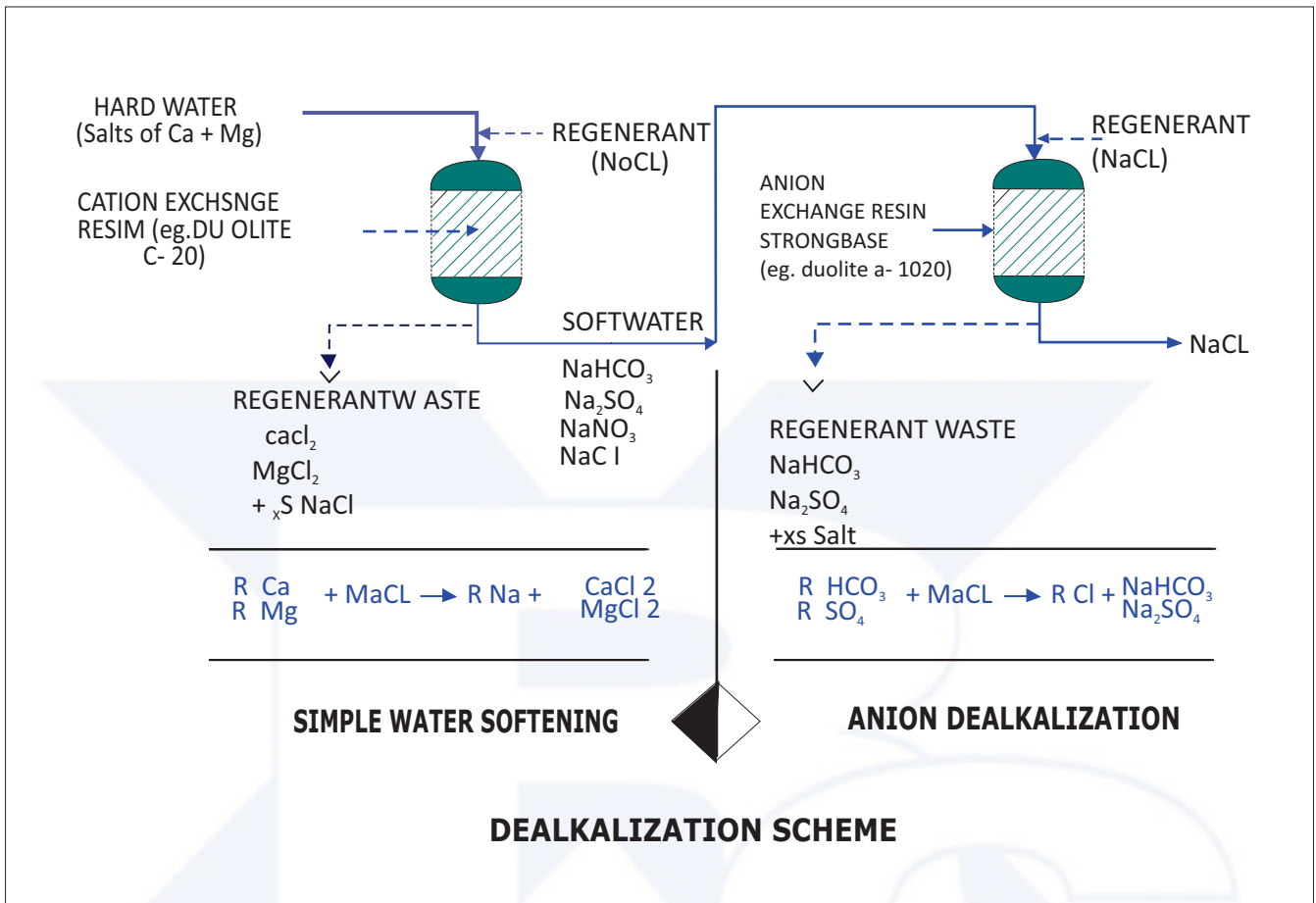
Adjusting the ratio of sodium zeolite effluent to hydrogen-cycle (acid) zeolite effluent obtains any desired alkalinity reduction. Split-stream dealkalization lowers the hardness level to nearly zero, reduces alkalinity and removes dissolved solids to the extent of alkalinity reduction.

Chloride dealkalization: Chloride dealkalization uses two ion exchange units operated in series. The first is a conventional sodium zeolite softener containing cation exchange resin, and the second is a dealkalization unit containing anion exchange resin. Both units are regenerated with salt, which eliminates the handling of acids required in the split-stream method. The sodium zeolite to remove hardness and the anion unit exchanges bicarbonate and sulphate for chloride. Alkalinity of the final effluent is reduced to nearly zero.

The chloride process does not remove dissolved solids or silica. All anions, including bicarbonate and sulphate, are exchanged, therefore, high-sulphate waters are costly to treat by chloride dealkalization. Because this process removes nearly all alkalinity, caustic soda is added to the system to obtain the necessary hydroxide alkalinity in the boiler water.

Chloride dealkalization is the simplest and most straightforward process as it eliminates the handling of acids required in the split-stream method.

A schematic representation of a chloride dealkalizer – with the reaction that take place—is illustrated in figure below:



Water Problem # 1 (Softening and De-alkalization):

When the total hardness to alkalinity ratio is less than one, a weak-acid cation is an effective way of treating water. Resin such as Duolite CC-3 is widely used in the industries, which simultaneously remove both hardness and alkalinity.

A weak-acid cation exchange resin is very useful where the hardness exceeds 3000 ppm. The scheme shown above is good for such a scenario.

Water Problem #2 (Softening and De-alkalization):

If the total hardness to alkalinity ratio is greater than one, the following scheme could be more effective to achieve complete removal of both hardness and alkalinity.

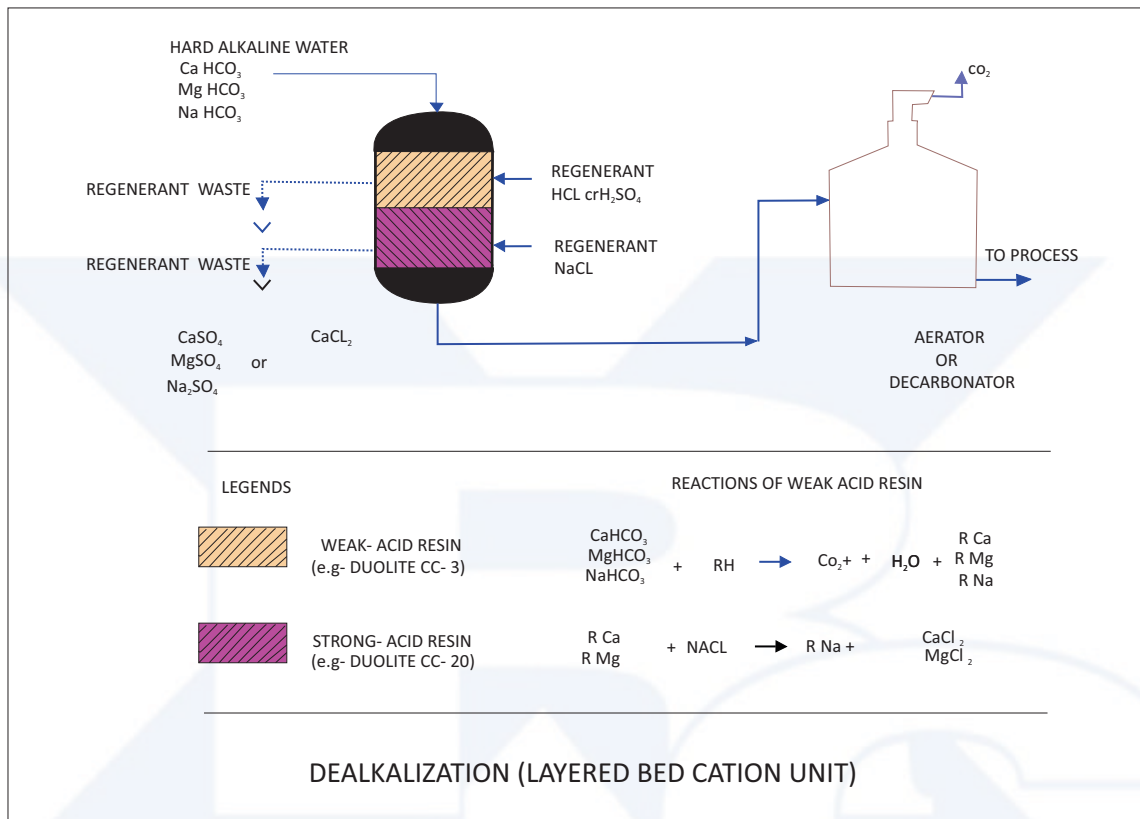
One of the commonly used techniques of producing soft, dealkalized water involves the use of layered-bed cation unit. This system consists of a single tank ion-exchange unit with a layer of lower density weak-acid resin on a layer of higher density strong-acid resin.

The weak-acid resin is regenerated with a mineral acid and the strong-acid resin with sodium chloride.

The weak-acid resin removes the temporary or carbonate hardness and the strong-acid resin remove the non-carbonate or permanent hardness.

The effluent from this duo-bed unit is then passed through an aerator or de-carbonator for removal of CO_2 .

The reaction of the individual resins are illustrated in figure below.



Note that the dealkalizer would seldom be used without a base-exchange softener, as the solution produced is acidic and would cause corrosion, and any permanent hardness would straight into the boiler.

DEMINERALIZATION BY ION EXCHANGE:

The demineralization (DM) process is primarily used where total dissolved solids (conductivity) is the limited feedwater constituent. This process will remove virtually all the salts to achieve water quality approaching distilled water. It involves passing the raw water through both cation and anion exchange resins. Sometimes the resins may be contained in one vessel and this is termed mixed bed demineralization. Demineralizers consists of ion exchange resin columns, a strong cation unit, and strong anion unit. Hydrogen cation exchange converts dissolved salts to their corresponding acid forms, which are removed by the basic anion exchanger.

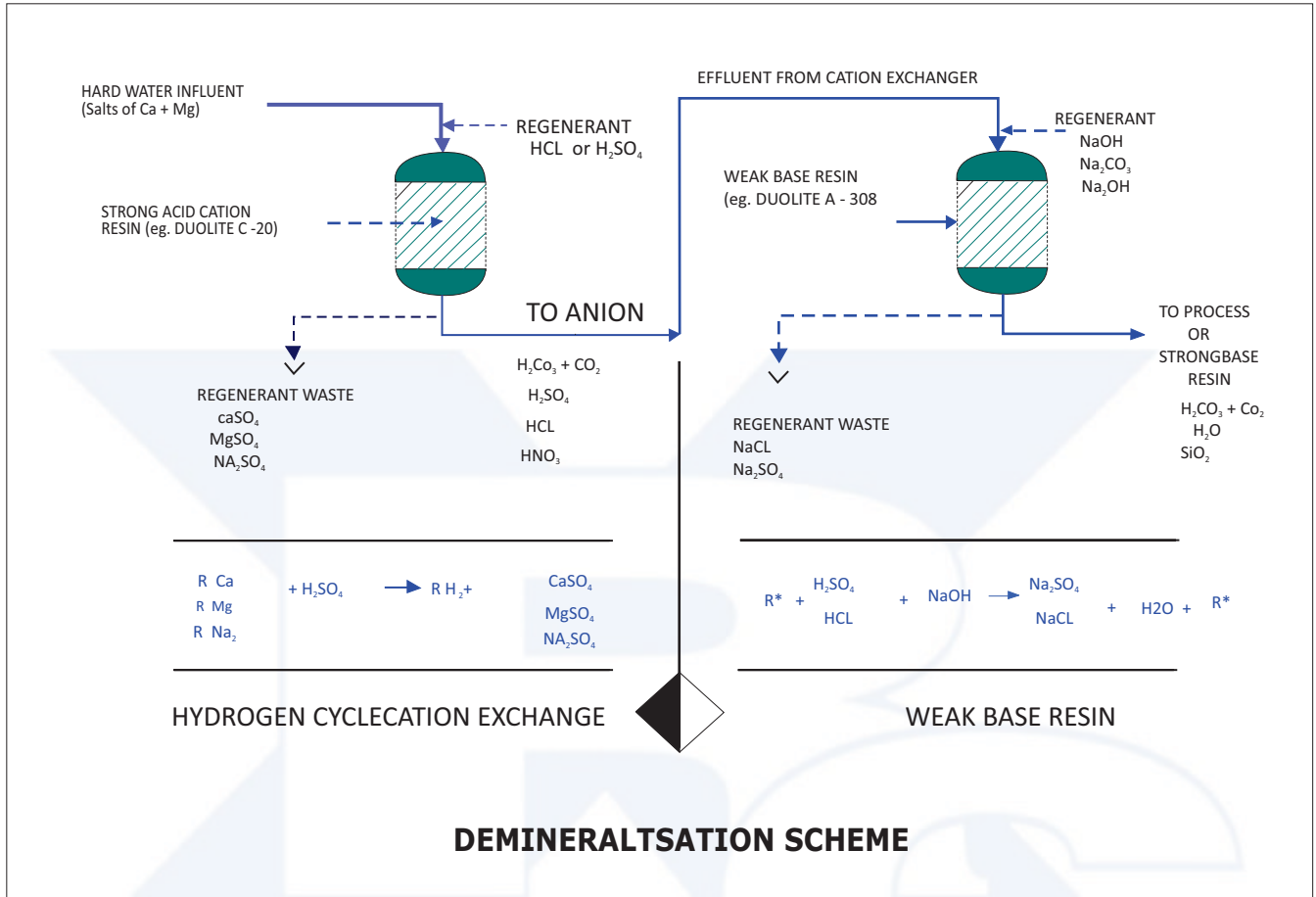
The cation exchanger in the hydrogen form exchanges hydrogen ions for the positively charged cations in the water. The effluent from such a unit is then carried forward to an anion-exchange resin.

The anion-exchange resin in the hydroxide form exchanges hydroxide ions for the anions in the water. This might be either a weak-base or a strong-base resin. A weak-base resin adsorbs the entire acid molecule and not just the chloride ion.

The process consists of a typical acid-base reaction, which forms the salt of that acid in water. In many applications, a strong-base anion resin follows the weak-base resin. The regenerant from the strong- base anion unit is sufficient to regenerate the weak-base anion resin in most cases.

The net result of this operation is replacement of the dissolved salts with water.

As mentioned before, it is possible to use many combinations of the various cation and anion-exchange resins to get the demineralized water.



DESILICIZATION:

Silicates cause another type of scaling and can be removed with ion exchange or a membrane process.

If silica is the limiting feedwater constituent, it is removed by strongly basic anion exchange resin regenerated with caustic soda. Two systems are used the choice depends on whether a reduction in the dissolved solids level also is required.

- 1) Desilicization uses a conventional sodium zeolite softener, followed by strongly basic anion resin unit. Hardness is reduced in the cation unit and all anions and silica are reduced to nearly zero.
- 2) A cation exchanger in the hydrogen form (regenerated with acid) is followed by a strong base anion exchanger (regenerated with caustic soda). All cations and anions are exchanged for hydrogen and hydroxide respectively, thus removing all dissolved solids, including silica to nearly zero. Demineralization results in a very pure effluent, but the cost of operation is high and may not be justified for low to moderate pressure boilers.

Desilicization using membrane systems is often preferred where dissolved ion concentrations are high because of operating cost considerations. High silicate levels are difficult and may require co-precipitation with other ions or high temperature caustic regeneration of ion exchange system.

DEAERATORS:

Mechanical deaeration is a process of eliminating O_2 and other corrosive gases from the feed water. Free CO_2 is also removed by deaeration, while it is released with the steam in the boiler and subsequently dissolved in the condensate. This can cause additional corrosion problems.

Since dissolved oxygen is a constant threat to boiler tube integrity, the discussion below aimed at reducing the O_2 content of the feed water. The two major types of deaerators are the tray type and the spray type. In both cases, the major portion of gas removal is accomplished by spraying cold makeup water into a steam environment.

Tray-Type Deaerating Heaters: Tray-type deaerating heaters release dissolved gases in the incoming water by reducing it to a fine spray as it cascades over several rows of trays. The steam that makes intimate contact with the water droplets then scrubs the dissolved gases by its counter-current flow. The steam heats the water to within 3-5 F of the steam saturation temperature and it should remove all but the very last traces of oxygen. The deaerated water then falls to the storage space below, where a steam blanket protects it from recontamination.

Spray-Type Deaerating Heaters: Spray-type deaerating heaters work on the same general philosophy as the tray-type, but differ in their operation. Spring-loaded nozzles located in the top of the unit spray the water into a steam atmosphere that heats it. Simply stated, the steam heats the water, and at the elevated temperature the solubility of oxygen is extremely low and most of the dissolved gases are removed from the system by venting. Time spray will reduce the dissolved oxygen content to 20 - 50 ppb, while the scrubber or trays further reduce the oxygen content to approximately 7 ppb or less.

For optimum oxygen removal, the water in the storage section must be heated to within 5°F of the temperature of the steam at saturation conditions. From inlet to outlet, the water is deaerated in less than 10 seconds. The storage section is usually designed to hold enough water for 10 minutes of boiler operation at full load.

What are important considerations in operation of Deaerators?

- 1) Heating of the feedwater- The operating temperature in the unit should be 227°F at 5 psi. The pressure/temperature relationship is important since deaeration must rapidly for quick and efficient removal of gases.
- 2) Agitation- Agitation is required to decrease the time and heat energy necessary to remove dissolved gases from the water.
- 3) Maximization of surface area- The water must be finely dispersed to expose the maximum surface area to the steam. This enables the water to be heated to saturation temperature more quickly and reduce the distance the gases have to travel to be liberated.
- 4) Venting- The liberated gases must be allowed to escape from the system as they are released.
- 5) There are few limitations. Inlet water should be virtually free of suspended solids that could clog spray valves and ports of the inlet distributors and the deaerators trays. In addition, spray valves, ports and deaerator trays may become plugged with scale that forms when being deaerated has high hardness and alkalinity levels. In this case, routine cleaning and inspection of the deaerator is very important.

Does the deaerator ensure complete protection against Oxygen?

Complete oxygen removal cannot be attained by mechanical deaeration alone. Equipment manufacturers state that a properly operated deaerating heater can mechanically reduce the dissolved oxygen concentrations in the feed water to 0.005 cc per liter (7 ppb) and zero free carbon dioxide. Typically, plant oxygen levels vary from 3 to 50 ppb. Traces of dissolved oxygen remaining in the feed water can then be chemically removed with the oxygen scavenger, usually catalyzed sodium sulfite. It is common practice to maintain a sulfite residual of 5-10 ppm in the feedwater and, if necessary, feed sufficient caustic soda or neutralizing amine to increase the feed water pH to between 8.0 and 9.0.

REVERSE OSMOSIS (RO SYSTEM)

Osmosis is the natural passage of a liquid through a semi-permeable, during which the liquid flows from a state of low concentration of solids or impurities to a state of relatively high concentration. Reverse osmosis is the reverse of the natural osmosis process that occurs in nature.

To treat water by the osmosis process, osmosis must be reversed to make the water from a state of high concentration of solids to a low concentration. This is done by applying pressure ranging from 400 to 2000 psig to the high concentration side of the membrane the result is high quality water.

It is a highly efficient method of obtaining high quality water & cost effective, particularly for situations where water TDS is above 2000 ppm.

Other Facts on Reverse Osmosis:

- 1) There are different theories about the water and salt transfer mechanism through the reverse osmosis membranes; one assumption is that capillaries are situated in the surface of the membrane through which the pure water flows another refers to a solution-diffusion phenomenon.
- 2) Reverse osmosis process does not allow the dissolved inorganic and organic matter to pass through the membrane or only to a very small extent. In addition, organic matter as well as colloids and turbidity are almost 100% removed.
- 3) Pure water is forced through the membrane and dissolved impurities remain on the feed side of the membrane.
- 4) The recovery rate or permeate typically ranges from 25% for small (100 gal per day) systems to 75% for larger (10000 gal per day) systems.
- 5) The single pass RO systems are employed where water TDS is about 150mg/l to 150mg/l.
- 6) Double pass RO systems are employed where water TDS is above 1500 mg/l.
- 7) Reverse osmosis process is generally preceded by thorough pretreatment filtration. A correct choice of pretreatment is very important as it influences the quality and quantity of the product, and above all, the life span of the module.
- 8) With increasing operating pressure and temperature of the water, the capacity of the Reverse Osmosis (RO) increases.
- 9) The capacity of the installation must be measured against the lowest feed water temperature. Since the rated output is based on 77 F (25 C), it must be divided by appropriate temperature correction factor.
- 10) Fouling can cause the capacity of the module to be reduced by about 20% at 400 psi (28 bars) and by 8% at 200 psi (14 bars) in three years.
- 11) An RO system typically reduces the silica concentration by 95-99% depending on the feedwater quality membrane used, water temperature and membrane arrangement.

In summary, there are various possible combinations and arrangement of ion-exchange resins to achieve reduction in hardness and/or dissolved solids. Each resin or combination is effective for controlling a particular parameter more effectively. It is recommended to consult water treatment equipment supplier for appropriate selection. The few resins are.

Resin	Function
Zeolite softener	To remove hardness i.e Ca, Mg
Weak Acid Cation (WAC)	To remove the weak acid cations, i.e hardness, Ca^{++} or Mg^{++} associated with alkalinity OH^- , CO_3^{--} , and HCO_3^-
Strong Acid Cation (SAC)	To remove the cations & anions including Ca^{++} , Mg^{++} , Na^+ , K^+
Weak Basic Cation (WBC)	To remove salts of strong acids, SO_4^{--} , Cl^- , NO_3^-
Strong Base Anion (SBA)	To remove all anions including SiO_2 and CO_2
Mixed Bed (MB)	It is a mixture of SAC and SBA resins. The function is to polish and remove residual remaining ions in water.

PART III CONDENSATE & BLOWDOWN WATER

Boiler feedwater consists of returned condensate plus the makeup water to satisfy steam demands. Uncontaminated condensate is low in dissolved solids and adds few impurities to the feed water. Makeup water usually contributes most of the contaminants therefore the more condensate recovered and returned the feedwater quality.

Condensate recovery is important to the overall efficiency of boiler for 2 main reasons.

- 1) Condensate is very high quality water. The more condensate that is returned, the less makeup water shall be used. The lesser the makeup water, the lesser shall be the amount of contaminants introduced into the boiler systems. The lesser the contaminants, the lesser shall be the need for both external and internal water treatment. This saves on the volume of the water on compensating makeup water and associated cost treatment/chemicals.
- 2) More the condensate recovery, lesser shall be the condensate that is discharged into a sewer system and lower shall be the blowdown. This shall reduce the sewer disposal costs.

Besides, lower costs on water treatment, condensate recovery leads to energy savings up to 10%. Condensate is usually very hot (130 to 225 F) compared to the temperature of makeup water (50 to 70 F). Losing hot condensate means losing precious heat equivalent to temperature differential of the makeup and condensate enthalpy.

Condensate recirculation is unsuitable only where there is possibility of condensate being contaminated because of process leaks and direct process contact. The contaminated condensate must be segregated from the pure stream, otherwise it may lead to bigger failures, safety and efficiency issues. It should be avoided.

Estimating % Condensate Return

On an ideal system, the condensate recovery could be worked out as below

As a rule, silica or neutralized conductivity tests on the boiler water sample provide a reasonable accurate basis for condensate return.

Consider, a test analysis on a small boiler using softened water indicate following analysis:

Location	Silica, ppm	Conductivity, micromhos (neutralized)
Boiler makeup	40	552
Condensate	3	45
Feedwater	20	265

Then based on silica results, the following equations can be used:

$$20 VF = 40VM + 3 VC \dots\dots\dots \text{Equation 1}$$

$$VF = VM + C \dots\dots\dots \text{Equation 2}$$

Where

VF= Volume of feedwater

VM= Volume of makeup water

VC= Volume of condensate

VC is estimated by solving equations 1&2 (multiply equation-2 with 3 and subtract from equation 1)

$$17 VF = 37 VM$$

From which:

$$VM = 17 \times 100 / 37 = 45.94\%$$

$$VC = 100 - 45.94 \text{ or } 54.06\%$$

Therefore In scenario above, the ideal condensate- makeup split is roughly 54% condensate and 46% makeup water.

If all the condensate streams return back to the boiler and nothing escapes the system, then the makeup water topping up is minimum. The process is essentially a “closed loop” process.

Most often, however, some water or steam escapes from the loop and makeup is necessary in order to maintain the water inventory. In the extreme case where no condensate is return to boiler, the process becomes a “once through” system and makeup water rate matches steam flow rate.

Generally the higher the makeup water, the higher shall be the impurities and higher shall be the water treatment costs. Closed loop process requiring minimum of makeup water is best way to ensure optimum level water quality.

Condensate Water Treatment an Monitoring:

Condensate water is very important to your facility and ignoring this unseen closed loop component will soon cause failures, costing bottom-line dollars. In general, the condensate is very pure, free of salts but it could be corrosive because it contains dissolved CO_2 and can add dissolved and suspected iron to the feedwater.

What is source of CO_2 in the condensate?

Carbonated and bicarbonate alkalinities in the makeup water break down under boiler temperature and pressure to form carbon dioxide (CO_2), which is liberated to the steam. During steam condensation, the carbon dioxide dissolved to form carbonic acid. If untreated, the condensate return piping, valves and tanks experience severe “grooving” corrosion. These products “neutralize” the acidic effects of the hot, carbonic acid.

What precautions are suggested for preventing against grooving corrosion?

The condensate system do not require elaborate external treatment as with makeup water but soft measures like condensate polishing or conditioning may be required to insure the integrity of your equipment.

The remedies and cautions are as follows:

- 1) The most common method of dealing with this problem is through the use of neutralizing amines. These chemicals, better known as morpholine and cyclohexylamine neutralize the carbonic acid, and increase the pH of the condensate.
- 2) A filming amine, such as octyldecylamine, provides a non-wettable protective barrier against both carbonic acid and oxygen. These create an oil attractive, water repellent film on metal surfaces which is resistant to both carbon dioxide and oxygen.

- 3) In order to minimize oxygen pitting, a volatile oxygen scavenger such as diethylhydroxyamine (DEHA) could be utilized. DEHA provides better results, as it scavenges oxygen and passivates or coats the condensate system, making it less susceptible to corrosion. Sodium sulphite and Hydrazine are other commonly used chemicals for oxygen scavenging.

A brief overview of chemical treatment is also covered in the next section.

BLOWDOWN WATER:

Even treated demineralized (DM) boiler feedwater contains small amounts of dissolved mineral salts. Ongoing water evaporator in steam boiler and fresh boiler makeup increase the concentration of these minerals and lead to the solids accumulation in either dissolved or suspended form.

- 1) Dissolved solids promote carryover of water with the steam, causing water hammer and damaging piping, or other equipment. Carryover also raises the moisture content in the steam, affecting proper operation of downstream equipment that uses steam.
- 2) Suspended solids cause sludge or sediment in the boiler. These affect the heat transfer capabilities of the pressure vessel and leads to problems ranging from poor fuel-to-steam efficiency to pressure vessel damage.

Chemical dosing of the boiler feedwater also leads to the presence of suspended solids in the boiler. These will inevitably collect in the boiler in the form of sludge, and are removed by a process known as bottom blowdown. Steam boiler should be down daily once or twice, to maintain recommended dissolved solids levels and to remove sludge and sediment.

Effects of insufficient or Excessive blowdown:

Insufficient blowdown may lead to carryover of boiler water into the steam, or the formation of deposits. Excessive blowdown will waste energy, water, and chemicals. The optimum blowdown rate is determined by various factors including the boiler type, operating pressure, water treatment, and quality of makeup water. Blowdown rates typically range from 4% to 8% of boiler feedwater flow rate, but can be as high as 10% when makeup water has high content.

For example, consider a 50000 lb/ hr boiler operating @ 125 psig has a blowdown heat content of 330 btu/lb. If the continuous blowdown system is set at 5% of the maximum boiler rating, then the blowdown flow would be about 2500 lb/hr containing 825000 Btu.

At 80 percent boiler efficiency, this heat requires about 1050 cu-ft / hr of natural gas, worth about \$42000 per year based on 8000 hrs operation per year at \$ 5 per 1000 cu-ft.

What is cycles of concentration?

Cycles of concentration refers to the accumulation of the impurities in a water supply.

When water is converted to steam, the dissolved solids do not travel with the steam, but are left behind in the boiler water. Fresh makeup water enters the boiler to replace the amount lost through steam evaporation. When this new water is converted to steam, more solids are left behind. As steam is continually produced, evaporated, and replaced with new water, the amount of solids in the boiler continues to increase indefinitely until the water is unable to dissolve its own impurities or hold them in solution.

For every pound of steam generated, a pound of water must be replaced. The amount of solids in the water will have doubled when the amount of new water that has entered the boiler is equal to the amount of water that was used to originally fill the boiler. When the amount of solids has doubled, there are 2 cycles of Concentration in the water, when the amount of solids has tripled, there are 3 cycles of concentration. Cycles of concentration is an indicator of the amount of solids buildup in the water.

Blowdown rate & Cycles of Concentration:

Blowdown limits the concentration of impurities in the boiler water. A boiler operating on high quality feedwater needs very little blowdown. The purer the feedwater, the lesser is the blowdown required and higher shall be the cycles of concentration. If the feedwater quality is improved so that it is concentrated 6 times rather than 3, the blowdown rate 100000 lb/hr steam boiler is reduced from 33.3 to 16.7 percent.

Increasing the cycles of concentration to twice the original value shall cut the blowdown and energy losses in half. One way to maximize the cycles of concentration of the boiler water is by controlling the boiler water at the highest allowable chemistry limits and feeding recommended levels of treatment. The quality of blowdown can be minimized and the steam purity maintained. In actual practice, a combination of the mechanical heat and chemical is best.

Example:

A 10000 lb/h boiler operates at 10 bar g- calculate the blowdown rate, if the maximum allowable boiler TDS is 2500 and the boiler feedwater TDS is 250 ppm.

The blowdown rate shall be governed by equation:

The blowdown rate = $\text{Capacity} \times \text{feedwater TDS} / (\text{Maximum allowable TDS} - \text{Feedwater TDS})$

Blowdown rate = $10000 \times 250 / (2500 - 250) = 1111 \text{ lb/hr}$

What parameters can be used to establish the cycles of concentration or regulating blowdown?

There are two tests used to establish the cycle of concentration or to regulate the frequency and volume of blowdown. These are chloride level and specific conductance.

Chloride Test:

Chloride is chosen as the indicator for cycles of concentration because,

- 1) It is always present in the makeup water.
- 2) It does not change character when heated.
- 3) It does not react with the chemicals in the water treatment, and
- 4) It does not leave the water in the boiler when steam is produced.

If the chloride in the water doubles, all the solids have doubled.

Example:

If the makeup chlorides are 20ppm and the boiler water chlorides are 100ppm, the boiler is at 5 cycles of concentration. If makeup chloride are at 30ppm and the boiler water at 120ppm, the boiler is at 4 cycles of concentration.

The chloride Test is run on a sample of the raw water and on a sample of the water from the boiler sight glass. When the chloride reading of the boiler water is 6 times the chloride reading of the raw water, there are 6 cycles of concentration.

Specific Conductance Test:

The second test used for regulating blowdown is specific conductance. A conductivity meter is used to measure the conductivity of the "make up" water as compared to the conductivity of the boiler water. The ratio of the two figures is the "cycles of concentration".

Example:

if the makeup water conductivity is 300 umhos and boiler water conductivity is 2100 umhos, $2100/300$ equals 7 cycles of concentration.

Important: in general, the boiler should never be operated over 10 cycles of Concentration.

Methods for controlling blowdown:

Blowdown systems could be either manually or automatically controlled.

- 1) **Manual control:** The amount of blowdown is determined by performing tests to determine the amount of dissolved solids in the boiler water. The operator must be thoroughly instructed in the correct blowdown procedure. Mud or bottom blowdown is usually a manual procedure done for a few seconds on intervals of several hours. It is designed to remove suspended solids that settle out of the boiler water and form a heavy sludge.
- 2) **Automatic blowdown:** The automatic controllers sense the boiler TDS in terms of electrical conductivity and automatically open or close the surface blowdown lines to control to exactly the right minimum level. The operator must check that the controls are set for required blowdown and that they are function properly. Automatic controls can have a significant impact on efficiency, especially if steam loads vary widely. Surface or skimming is designed to remove the dissolved solids that concentrate near the liquid surface. Surface blowdown is often a continuous process.

PART IV CHEMICALS FOR BOILER WATER CONDITIONING

Internal water treatment is usually still required to supplement the external treatment (for example, the base exchange system) and is generally carried out by adding chemicals in metered amounts, into either the feedwater tank or the feedwater pipeline prior to its entry into boiler.

The objective of internal water treatment are:

- 1) To prevent scale formation from low remaining levels of hardness that may have escaped treatment. Sodium phosphate is normally used for this, and causes the hardness to precipitate to the bottom of the boiler where it can be blown down.
- 2) To deal with any other specific impurities present.
- 3) To prevent corrosion while maintaining the correct chemical balance to remove traces of dissolved gases primarily O_2 and CO_2 that may have escaped deaerator.

Thus the main purpose of the internal treatment is to ensure quality because, inevitably, there will be some impurities that find a way through the main external treatment system.

Various chemical formulations are available from water treatment companies to control individual parameters such as alkalinity. Sulfite, dispersant, condensate pH, etc; and , variety of multipurpose (one-drum) formulations. Principally, any of these formulation aim at changing scale/corrosion forming salts into soft or mobile sludges . The sludge conditioners used In the chemical dosing prevent these solids from depositing on metal surfaces and keep them in suspension. It is important to note that the chemicals added during the conditioning treatment will increase the TDS level in the boiler water and higher rate of blowdown will be required.

The common types are listed below:

Alkalinity Adjunct Formulations:

Boilers require a certain amount of hydroxyl (OH^-) alkalinity to prevent corrosion and help maintain clean heat transfer surfaces. Where makeup water alkalinity is low, these formulations provide needed alkalinity.

- 1) Liquid alkalinity adjunct with polymeric dispersant.
- 2) Concentrated, liquid alkalinity adjunct.
- 3) Liquid alkalinity adjunct with polymeric dispersant and sludge conditioner.

Ploy-phosphate Formulations:

For boiler systems with trace of hardness in the feedwater or with un-softened makeup water, the phosphate formulations “sequester” the hardness salts and prevent hardness scale from on the heat transfer surfaces. These basically extend the solubility limit of calcium. The phosphate-polymer programs can essentially handle any feed water hardness and be cost effective. This is particularly true of the new synthetic polymers. These are normally available as:

- 1) Concentrated polyphosphate formulation.
- 2) Polyphosphate formulation with sludge conditioner.
- 3) Polyphosphate with sludge conditioner, dispersant and alkalinity adjunct.
- 4) Polyphosphate with terpolymer, dispersant, and alkalinity adjunct.

The main limitations of these are that in case pH increase beyond 7.3 these will be converted into orthocompound, which will react with calcium and form the sludge. Polyphosphate formulation with sludge conditioner may be the answer to such conditions. Generally, a phosphate-treated boiler leaves a light grey deposition of approximately 1/16 inch. The rolled tube ends the steam drums frequently have larger amounts of deposition. Sludge is evident in the mud drum and this deposition is easily water washed.

Sodium Meta Phosphate (SHMP):

This is effective in a sense that it delays the solubility limit of calcium and therefore the scale formation is delayed. The disadvantage however is that it degenerates into ortho-compound and require pH to be controlled with in 6.5 to 7.4. it also acts as food for bio fouling. The latest developments are employing amino trimethylene phosphate acid (ATMP) and Hydroxyl Ethylkedene di-Phosphate Acid (HEDP) that does not the limitations of SHMP.

Sludge Conditioners/Dispersants

Synthetic organic polymer formulations are used to disperse suspended solids in the boiler water for removal by surface and bottom blowdown. By maintaining proper concentrations of the sludge conditioner/dispersant, the heat transfer surface remain free of deposition and maintain high heat transfer efficiency. By maintaining high concentrations of certain products, old scale can be removed on line. These are normally available as:

- 1) Concentrated homopolymer/alkalinity adjunct.
- 2) Concentrated homopolymer sludge conditioner with anti-precipitant.
- 3) Concentrated terpolymer sludge conditioner with anti-precipitant.
- 4) Concentrated terpolymer sludge conditioner with anti-precipitant.
- 5) Concentrated terpolymer sludge conditioner.

Oxygen Scavengers:

Oxygen scavengers are needed to prevent oxygen-pitting corrosion in the deaerator, feedwater tank and boiler vapor space. These products chemically “scavenge” the dissolved oxygen and prevent corrosion. These products can be inorganic or organic, catalyzed. The common oxygen scavengers are available as:

- 1) Dry, un-catalyzed sodium sulfite
- 2) Dry, catalyzed sodium sulfite
- 3) Dry, catalyzed, de-characterized sodium sulfite
- 4) Liquid, catalyzed sulfite
- 5) Liquid, catalyzed metabisulfite
- 6) Liquid, catalyzed sulfite/metabisulfite
- 7) Liquid, hydrazine
- 8) Liquid, hydroquinone
- 9) Liquid, diethylhydroxyamine (DEHA)
- 10) Liquid, methyl ethyl ketoxime

All the above types remove even trace amounts of oxygen.

The most common oxygen scavenging compound is sodium sulphite. 8 ppm of sodium sulphite is sufficient to deal with 1 ppm of dissolved oxygen. However, it is practice to add an extra 4 ppm of sodium sulphite because:

- There is a significant danger of corrosive damage.
- The chemical dosing system is usually 'open loop' with water samples taken at intervals, and adjustments made to the dosing rate.

- There is a concern about complete dispersion of the chemical, perhaps due to the method of injection, circulation currents, or stratification within the feed tank.

The total dosing rate, therefore, is 8 ppm of sodium sulphite per 1 ppm of dissolved oxygen plus 4 ppm.

Other oxygen scavengers involve organic compounds or hydrazine. The latter, however, is carcinogenic, and is not generally used in low and medium pressure plants.

Boiler Antifoam Formulation:

Some boiler exhibit a tendency for foaming and carryover due to condensate contamination or high alkalinity/ total suspended solids. These formulations provide a means to prevent foam from forming in the boiler. Various concentration of boiler antifoam depends on boiler size.

Alkaline Boil-out Formulations:

New boiler require "boil-out" to remove oil/grease, dirt, and other organic contaminants from the water side of the heat transfer surfaces. These formulations are designed to provide cleaning and passivation of these surfaces. These formulations are available as:

- 1) Concentrated, alkaline, polyphosphate for de-oiling and passivation.
- 2) Concentrated, alkaline, peptizing agent, dispersant for de-oiling and foulant removal.
- 3) Concentrated, low cloud point, nonionic surfactant for heavy oil and grease removal.

Condensate Return Line Formulations:

Carbonate and bicarbonate alkalinities in the makeup water break down under boiler temperature and pressure to form carbon dioxide (CO₂) which is liberated to the steam. During steam condensation, the carbon dioxide dissolves to form carbonic acid. If untreated, the condensate return tanks, valves, and piping experience severe "grooving" corrosion. These products "neutralize" the acidic effects of the hot, carbonic acid. The remedies include:

- 1) Low distribution ratio amine blends in demineralized water
- 2) High distribution ratio amine blends in demineralized water
- 3) Low and high distribution ratio amines blended in demineralized water
- 4) Low, medium, and high distribution ratio amines blended in demineralized water
- 5) Medium distribution ratio amine blended in demineralized water.
- 6) Very high distribution ratio amine blended in demineralized water
- 7) Low, medium, and high distribution ratio amines with a volatile oxygen scavenger blended in demineralized water

Carbon dioxide protection:

Dissolved carbon dioxide is often present in feedwater in the form of carbonic acid resulting in lowering of the pH levels. Alkalinity levels in the boiler are particularly important. Maintaining a pH level of 10.5 to 12 will avoid corrosion problems by providing stable conditions for the formation of a film of magnetite (Fe₃O₄) in a thin, dense layer on the metal surface, protecting them from corrosive attack.

proper pH control by the addition of sodium hydroxide will correct this, but carbon dioxide is also released in boilers due to heating of carbonates and bicarbonates. These decompose into caustic soda with the released in boilers due to heating of carbonates and bicarbonates. These decompose into caustic soda with the release of carbon dioxide.

This is usually dealt with by use of a condensate corrosion inhibitors usually neutralizing & filming amines.

- 1) The most common method of dealing with this problem is through the use of neutralizing amines. These chemicals, better known as morpholine and cyclohexylamine neutralize the carbonic acid, and increase the pH of condensate.

- 2) A filming amine, such as octyldecylamine, provides a non-wettable protective barrier against both carbonic acid and oxygen. These create an oil-attractive, water-repellent film on metal surfaces which is resistant to both carbon dioxide and oxygen.

Multipurpose Formulations:

Multipurpose Formulations are often used for smaller boiler systems requiring simplicity in the treatment approaches. The multipurpose formula provides a preventive relief to various combinations, whether it is:

- 1) multipurpose formula for treating small systems with softened makeup and significant condensate return (neutralizing amine included)
- 2) Multipurpose formula for treating small systems with hard water makeup and significant condensate return (neutralizing amine included)
- 3) Multipurpose formula for treating small systems with hard water makeup and little or no condensate return (no neutralizing amine)

These multipurpose formulations are generally used where less detailed water analysis is available. This is however a risky and not a recommended option for long run.

Case Example:

One facility was found to be using a low pressure boiler water treatment product for a higher pressure boiler with a steam super-heater and steam turbine, which required high purity steam. Super-heater tube failure frequency was increasing. The treatment product contained phosphate treatment chemical in potassium, rather than the anticipated sodium form. Steam purity studies using standard sodium electrode procedure indicated acceptable steam purity. Analyzing for potassium, and then modifying the boiler water treatment program to use sodium-based phosphate treatment, enabled a corrosive steam solids contamination to be identified and controlled through improved boiler water level control.

Conclusion:

It is important to note that the water treatment/conditioning shall be evaluated case to case basis depending on the impurities inherent in the makeup water, its hardness, volume of condensate returned for reuse, quality of feedwater (makeup + condensate) and also on the design of boiler and its operating conditions. Deciding on the type and amount of chemical and water treatment system is a matter for a skilled water treatment specialist who should always be consulted.

Further detail on this complicated subject is available from water treatment handbooks and water treatment specialists; this is very much a matter for expert advice and professional analysis.