CHAPTER – 17
Boiler Water chemistry and Chemical Treatment

Introduction

Boiler is a vessel wherein water is heated to convert into steam, with the application of heat of a burning fuel and/or the hot exhaust gas from some process. The heat potential available in steam is one of the well-known sources of energy to do mechanical work in any steam engine. It is essential to maintain uninterrupted flow of steam to the engines and hence the boiler has to be necessarily fed with adequate supply of water to keep up a safe level in the drum. In order to ensure long life and trouble free operation of a boiler it is important to keep the boiler water chemistry under control. Depending upon the working pressure and temperature of boiler, the quality of Feed Water for the boiler is to be maintained. However, due to continuous evaporation occurring in boiler, the concentration of impurities in the boiler goes on increasing. Therefore, it is necessary to carry out chemical injection in the boiler for forming precipitates of impurities, which are to be drained out at regular intervals. Due to this regular draining or blow down the quantity of water in boiler system has got to be continuously made-up by feeding high purity water which is obtained by appropriate treatment of raw water.

Natural Water:

Though the water, in nature, is available in plenty, it can not be taken for use in a boiler without a proper chemical treatment. The physical and chemical properties of natural water, which widely vary, depending upon the source and strata on which it flows, makes it unsuitable for direct use in a Boiler. The natural water picks up minerals and salts from the earthen layer, which gets into the solution. Water, therefore, is a mixer of composite mineral salts in dissolved condition, in varying proportions, composition and degree. It gets polluted further with multifarious organic and inorganic impurities, due to disposal of industrial and domestic wastes. Decayed vegetation and marine lives also contribute to water contamination. Not only the dissolved salts in water, but also the presence of the coarse and undisolvable substances in suspended form, constituting mainly of silt and clay matters, generally termed as turbidity, make it unsuitable for direct use, without any treatment. Natural water, found on earth, contains siliceous matters, in dissolved as well as in colloidal forms, the proportion of which varies depending mainly on the following conditions:

a) pH
b) Chemical characteristics of the particulate
c) Seasonal conditions
d) Marine life
e) Temperature
f) Stagnation or Velocity of the flow.

Impurities:
Dissolved impurities:
Mainly the dissolved solids found in water are mineral salts. These contaminants in water exist as salts of calcium, magnesium and sodium, predominantly in the form of bi-carbonates, carbonates, chlorides and sulphates. To a lesser extent, potassium and iron salts are also present. Nitrates and silicates of such substances are also found to a small degree. Very rarely, Phosphates and a few heavy metals are also found in natural water. The quantity and composition of the solids present depend upon the soil and strata details and the origin of water. For instance the quality of river water is subjected to wide variations depending on seasonal changes. Similarly the qualitative and quantitative inflow of industrial and domestic wastes also influence the physical property of water and the chemical composition of the salts. Out of all such contaminants, sodium and organic contents vary very widely.

Various gases, mainly Oxygen, and others like Carbon dioxide and Hydrogen Sulfide are normally present in dissolved form and the presence of such dissolved gases alter the composition and concentration of certain salts.

Dissolved Oxygen:

Dissolved oxygen plays significant role in boiler feed water. The oxygen accelerates corrosion of water tube material. Mainly oxygen is removed only in Dearetor. Hence performance of Dearetor is very important.

Deaerator performance has to be maintained limiting dissolved oxygen to less than 0.01 ppm level. A figure < 0.007 ppm is considered to be very ideal.

Total Solids:
The basic idea is to restrict impurities in feed water as low as possible in order to avoid rise in boiler water concentration and deposition of metal oxides in the boiler. Moreover, since feed water is used as spray media for attemperation, TDS plays a very vital role in preventing super heater and turbine blades fouling.

Organic Matter:
It is very difficult to eliminate organic matter totally from water. Presence of organic matter is due to poor pretreatment practice, ineffective D.M. plant performance, resin leaking or condenser leakage. Quality of raw water at intake point is a deciding factor. Seasonal changes play a vital role.

Chlorides:

Presence of chloride in feed water is harmful to the system as whole. Hence it is very advisable to limit chloride concentration in feed water, keeping in mind, limit prescribed for boiler water and restriction as per drum pressure ratings. Leak proof condenser and efficient demineralization are essential prerequisites to avoid contamination due to chloride. Dosing chemicals fed to the drum can contribute in sizeable proportion to chloride contamination if the chemicals are not of adequate quality. Very low level chloride should be tested by selective ion electrode for accuracy.

Suspended and colloidal impurities:

Clay and sand particles constitute a major portion of the suspended matter. Very fine clay remains in colloidal state. Colloidal suspension of dye material and certain organic contents, give colour to water, in most cases.

General nature of dissolved contents:

Normally the mineral salts dissolved in water are found to exist in the ionized form. Generally there is no uniformity in quantity and proportion of such dissolved salts, since their presence is mainly dependent on the sources of the water. However fair representations of composition of mineral salts, as widely found in nature are brought out below:

CATION (Basic Radical)	ANION (Acidic Radical)
Ca^{++} (Calcium)	HCO_3^- (Bicarbonate)
Mg^{++} (Magnesium)	CO_3^{--} (Carbonate)
Na^+ (Sodium)	SO_4^{--} (Sulphate)
Fe^{++} (Iron)	Cl^- (Chloride)
Al^{+++} (Aluminium)	NO_3^- (Nitrate)
	PO_4^{---} (Phosphate)
	SiO_2 (Silica)

Definitions
pH:

pH is the logarithmic reciprocal of the Hydrogen Ion Concentration in a solution. It is expressed as integer. If pH is 7, the fluid is neither acidic nor alkaline, it is the neutral state. If the pH is less than 7 it is acidic in nature. If the pH is more than 7 it is alkaline in nature.

As N_2H_4 (Hydrazine) and N_2H_4OH dosing is done at the feed water suction line of the feed pump. Some times the pH dosing is also done in the condensate line before it goes to Dearetor. So improvement of pH in boiler feed water starts before it reaches Dearetor or just it leaves the Deaerator. In order to give protection to feed line and economizer, against low pH or oxygen corrosion, feed water pH requires to be maintained high. But in case H.P. heater elements are of copper alloy, it is advisable to restrict pH towards lower limit in order to ensure copper carry over is not taking place. Upper limit is prescribed for H.P. heaters of steel elements alone. This point should be clearly kept in mind.

The intensity of acidity or alkalinity of aqueous solutions or extract is determined by the amount of hydrogen ion or hydroxyl ion. It should be clearly understood that pH is not a constituent or impurity of the water. It is a figure representing the concentration of hydrogen ions in the water produced by various chemicals dissolved in it. As it is, water contains hydrogen and hydroxyl ions from the dissociation of water molecules.

$$H2O \rightarrow (H+) + (OH-)$$

D - 3
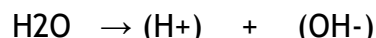
The product of hydrogen ion concentration and hydroxyl ion concentration is always a constant. The unit of measurement of ionic concentration is gram ions per litre. In pure water the concentration of hydrogen is 0.0000001 gm/ltr of water. In neutral water this is exactly balanced by hydroxyl ions.

The more the hydrogen ion concentration, the more acidic is the solution. At 25 °C, in case of pure and neutral water, which is neither acidic nor alkaline, the mathematical product of hydrogen and hydroxyl ion concentration is always a constant and is equal to 10^{-7} . Negative value of the Logarithms of the hydrogen ion concentration is used to express pH, indicating degree of acidity or alkalinity.

$$pH = - \log [H+]$$

Conductivity:
Conductivity is measured at 25 °C at local continuous flow sampling point at the down stream of a strong cation exchanger with a closed cell provision having no access to atmosphere. The figure is relevant for CO_2 free sample only. In case, combined CO_2 is present, conductivity through cation column will be higher in proportion to the CO_2 concentration. In such cases correction applied for CO_2 will give fairly reliable figures.

Water as feed to boiler:

We have seen that water as available in nature cannot be used directly in boilers for raising steam. It has to be treated and chemically conditioned to render it fit for use as feed and make up in the steam generation process. Mechanical and chemical treatments are the primary steps to make it free from suspended, colloidal and dissolved impurities, so that it attains perfectly pure status. It is the process of pre-treating and de-mineralizing the water to make it fit for use in any boiler.

However, in the actual process of steam generation, it is required to further chemically treat the water at various stages in order to make it suitable as a feed to a boiler, which will be non corrosive and protective to various ferrous and non ferrous alloys, deployed in the design and construction of various equipment. In a nutshell, treatment and further conditioning of water are necessary for the following objectives:

a) To prevent scaling internals of pressure vessels due to dissolved and suspended impurities,

b) To prevent corrosion of metallic parts of the boiler, with which water / steam come in direct contact,

c) To establish protective coating over metallic surfaces to prevent corrosion attack.

d) To avoid salt deposits over turbine blades,

e) To ensure better utilization of heat energy and to improve on efficiency,

In order to ensure to achieve above objectives, following processes of water treatment are adopted:

1. Pre treatment

2. Demineralization
3. Chemical conditioning

Pretreatment of water:

Clarification:

Pre- treatment to raw water is mainly to make it suitable for further processing of water by Deionization units. The water entering Demineraliser plant should be free from suspended, colloidal and organic impurities and the process of pretreatment plays a vital role in ensuring proper feed input is made to Deionization units. Presence of such suspended impurities adversely affects the deionization properties of the resins, which will affect the end quality of Demineralized water. Suspended & colloidal particles are removed by clarifying the water in a clariflocolator aided by suitable coagulating agents. It is further chlorinated to achieve effective oxidation to combat organic contamination. Depending upon the quantum and concentration of dissolved solids in raw water, partial softening and removal of silica is also to be achieved in pretreatment process. This is done in Precipitator Clarifier Section.

Precipitator Clarifier Section:

A precipitator inlet flow control valve controls the raw water inlet flow into the clarified water basin, through a level controller. A manual by-pass valve is also provided to the level control valve, so that in case of problem in the level control valve, manual operation can be done to maintain the level. The precipitator is of a reinforced concrete construction, in the shape of a truncated conical vessel placed in inverted position, with a circumferential channel all around the bigger diameter section at the top (Fig. 1). The conical concrete tank consists of a cylindrical tank built internally at the central portion. The inner cylindrical compartment is known as the flocculating mixing-zone and the outer compartment, the sedimentation sludge blanket zone. The raw water enters the inner mixing zone through an open channel from the top and flows downward into the inner conical tank.
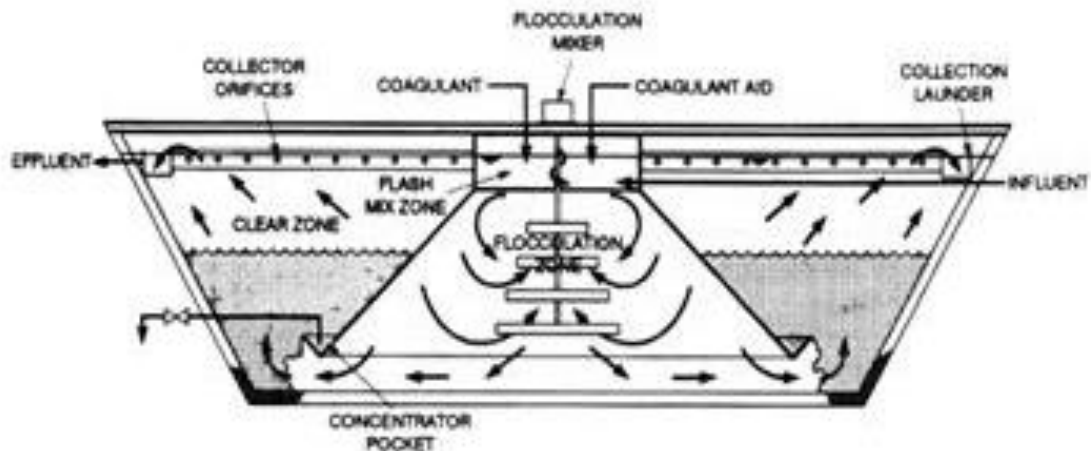

Fig. 1

The precipitator is fitted with a carriage, which can slowly be driven to go round inside the Clariflocculator. The carriage carries a paddle mechanism, with three or four tiers of vanes fixed vertically down and hanging from the paddle mechanism. The carriage is driven by an electric motor and a gear mechanism, with its axis at the center of the conical tank and the other end of the carriage placed with a wheel over a circular rail, fitted along the circumference of the conical tank. When the carriage is driven by the motor it goes round and round the top of the conical tank in a circular motion and the paddle mechanism stirs well the water in the outer conical zone. Chemicals, Alum and Lime, solutions are prepared in separate tanks and the prepared solutions are pumped trough pumps. The chemicals are let into the open channel to get mixed thoroughly with the raw water flowing along the open channel into the mixing chamber. A water flow indicating mechanism is fitted in the open channel to indicate the raw water flow.

The "precipitator" operates on the "sludge blanket" principle, whereby a bed of sludge particles is retained in suspension at a predetermined level in the outer cone. The slow speed agitator ensures thorough mixing of chemicals and raw water and assists in the completion of precipitator chemical process. The blanket consists of a loose mass of suspended floc constituting of medium sized particles. These attract and retain finer particles rising through the blanket, so that, when the water rises above the blanket zone, it is filtered and is almost clear. Above the blanket zone, some particles of floc remain but these continue to grow and fall back so that water decanting through blankets of sludge and rising to the top of the "precipitator" is almost free from floc and turbidity. The clear water overflows through the notches and falls into the circumferential channel and from there through open canal flows into the clarified water tanks. The clarified water may still have some traces of undesolved, suspended chemicals and precipitates. Such traces of suspended particles are further removed by filtration passing through the pressure sand filters. The circulating pump insures a more efficient reflux of sludge, particularly at low throughput. Continuous spent large floc desludging of the concentrator on the precipitator is carried out through a pneumatically operated valve which is set to open at regular intervals. 2(two) valves are provided for draining the precipitator.

Ferrous sulphate solution is delivered into the "Precipitator" by means of twin head proportional feed 5% solution dosing pump.
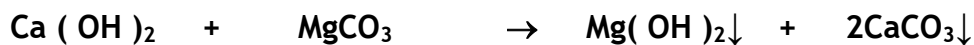
(The concentration values for both Lime and Ferrous sulphate dosage for precipitator   change according to raw water quality and will be recommended by the Original Equipment supplier.)

Chemicals are dosed proportionally to the raw water flow rate by an automatic proportioning system consisting of a flow recorder control totalizer and low flow alarm, which regulates the stroke of the ferrous sulphate pump and the swing angle of the lime dosing device respectively.

The raw water is treated in the precipitator with hydrated lime for removal of temporary hardness, caused by bicarbonate in Calcium and Magnesium salts. Hydrated lime reacts chemically with the bicarbonates of Calcium and

Magnesium salts in the water, forming a sludge of calcium carbonate and magnesium oxide, which gets settled down in layers. Alum, chemically known as Ferrous Sulphate is also added along with lime dosing, in the clariflocculator to hasten the process of coagulation and assist in settling of the sludge. The following chemical equations illustrates the chemical reaction of lime with the calcium and magnesium bicarbonates:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$

$$2Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3\downarrow + 2H_2O$$

$$Ca(OH)_2 + MgCO_3 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow$$

The chemical reaction of Ferrous Sulphate with calcium bicarbonate is as illustrated below:

$$4FeSo_4 + 4Ca(HCo_3)_2 + O_2 \rightarrow 4Fe(OH)_3 + 4CaSo_4 + 8Co_2 + 12H_2O$$
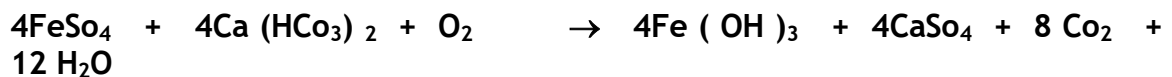
(Insoluble)

The colloidal produced by Ferric Hydroxide in this reaction is negatively charged, and is an effective coagulant of the positively charged, colloidal precipitates formed in the reaction of Lime with salts causing temporary hardness. A moving carriage slowly rotates, stirring the water and helps in creating an effective reaction of chemicals and settling down. The precipitated chemical in this reaction with the Calcium and Magnesium salts, form an effective sludge in layers, which can be easily removed by blowing down. However this sludge is slightly soluble in nature and in small quantities, always remains in solution with clarified water. Whatever the residual calcium, magnesium and sodium salts and silica still present in the clarified water are removed by the successive ion exchange process with the resin beds in the water de-mineralizing plant.

Filtration:
Water filtration is the process of separating suspended and colloidal impurities from water by passage through a porous medium. A bed of granular filter material or media is used in most plant application.

A filter may be defined simply as a device consisting of a tank, suitable filter media and necessary piping, valves and controls. Filters are designed for the following:

- Gravity flow, with natural head of water above the filter bed and low point of discharge at the filter bottom, providing the pressure differential needed to move the water through the filter bed.

- Pressure units, which, as their name implies, are operated on line, under service pressure, filtering the water as it flows the tank on its way to service or storage

Filters are classified in a number of different ways – by type or kind of filter medium to be deployed, such as sand, anthracite coal, activated carbon, fabric or porous membranes, or, by the direction of flow – upflow or downflow. Also, they are sometimes described hydraulically as the slow rate or rapid rate type. Varied design and process techniques are adopted based on the quality and the quantum of the raw water, to be treated and the quality of the effluent to be achieved. Economy is a vital point to reckon with. Sand Filters are used for this purpose.

Gravity Filters: Gravity filters are usually employed where large quantities of filtered water are required. It normally use 8 to 12 feet high tank constructed of steel or concrete. Concrete tanks are usually rectangular; steel tanks are round or rectangular. The end of gravity filter runs is usually determined by the head loss or pressure loss developed across the filter bed, and backwashing is initiated on this basis. Water quality deterioration (turbidity breakthrough) can also be used.

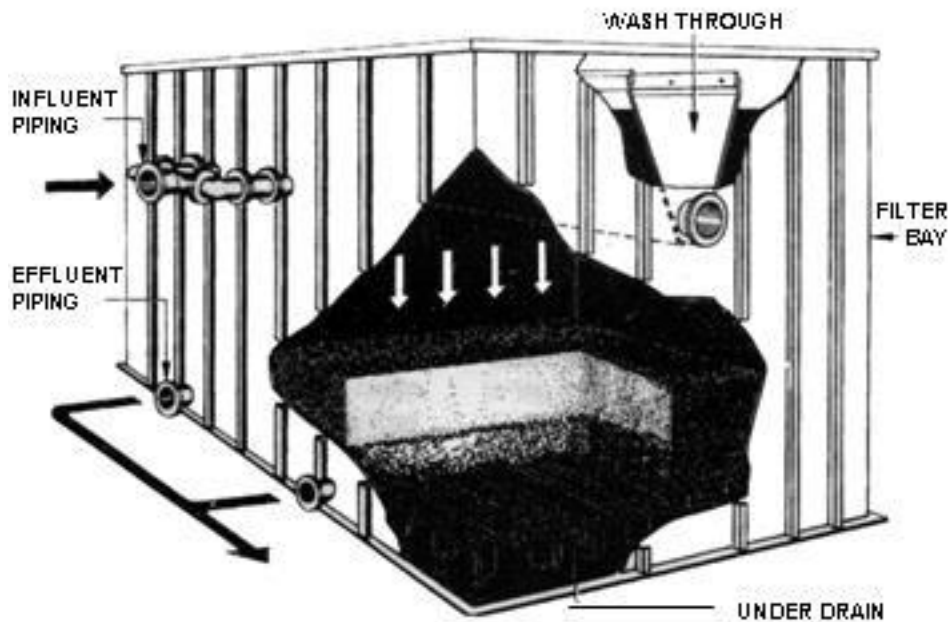Fig. 2 below shows a typical rectangular gravity filter.

Fig. 2

Pressure Filters: Three basic types of Pressure Filters are: Vertical Downflow, Horizontal Downflow and Vertical Upflow. Vertical and horizontal downflow pressure filter units are the 'work horse' of the filtration field and most widely used.
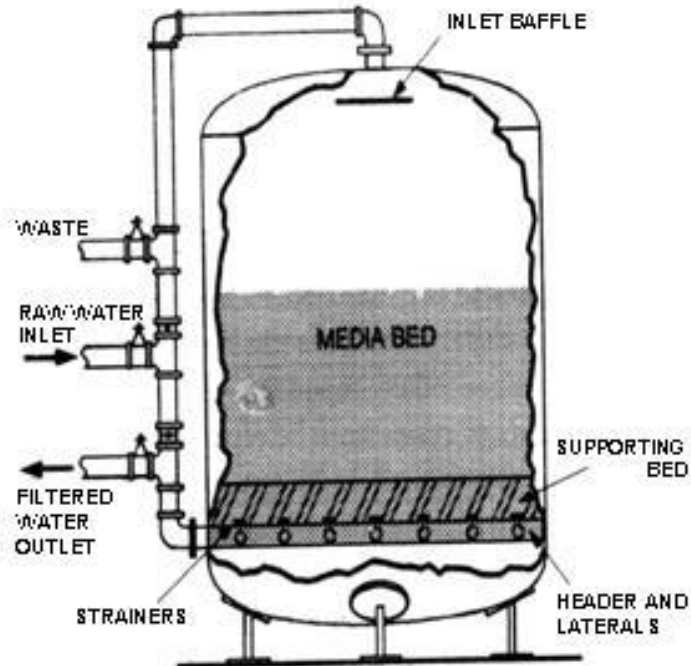
Fig. 3

Vertical Downflow Filter: In a vertical downflow filter, unfiltered water enters the top of the filter tank and flows downward through the bed of filter medium., wherein the suspended matter is removed. The filtered water is collected at the bottom of the tank and delivered to service. A typical downflow pressure filter is shown in fig. 3 above.

Horizontal downflow filter: As the name implies, a horizontal downflow filter deploys the filter tank in a horizontal position. Otherwise, the operation is identical to that of the vertical type. By using the filter tank in horizontal position, a large bed area is obtained, thus increasing the flow rate available from a given tank size.

Clarified water Pumps take suction from the clarified water basin and pump the water through the filters. Each pump is complete with motor, isolating valves, non return valves, manometers and accessories, pump water under pressure through the filter beds. The water flowing out of pressure sand filters goes into a filter water storage tank. Collection of excessive sludge and suspended materials get accumulated in the sand filter beds and causes resistance to flow resulting in head loss of flow of water.

Backwashing: When differential head between inlet and outlet increases, the filters must be taken out of service and backwashed for removing accumulated dirt and sludge materials. The filters are nevertheless to be backwashed at least once every operating day. For back wash the flow direction is reversed that is the inlet is given at the bottom and water from the top is delivered out to open canal. When the water flows in reverse direction it carries all the

accumulated dirt and sediments and throws out along with the water. The back washing is to be done until the out flowing water is perfectly clear of all accumulated sediments.

Chlorine removal:

To avoid algae formation chlorine is dosed into raw water, before the process of clarification in the clariflocator. Presence of chlorine is harmful to the Ion Exchange Resin and it is essential to ensure that even the traces of chlorine are not present in the clarified and filtered water, before admission to deionizing unit. Hence before admission to cation vessel, the water is once again filtered treated in a vessel containing a bed of Activated Carbon. Activated Carbon Bed absorbs left over chlorine and the organic matters and feeds clear water to the ion exchange vessels.
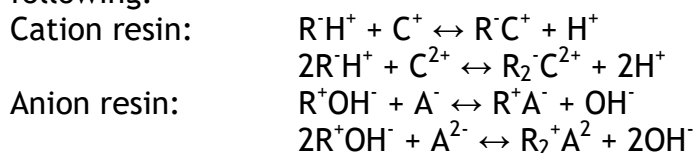
Demineralization:

Demineralization is the removal of dissolved ionic impurities that are present in water. Demineralized water is commonly produced by one or a combination of the following processes:

• Ion exchange
• Membrane desalination
• Thermal desalination

The method selected to produce demineralized water depends on the quality of the influent water, the required quality of the effluent water, the availability of resources such as regenerant chemicals, and wastewater treatment and disposal requirements. The economics of the processes that produce acceptable effluent quality must be evaluated to determine the most cost-effective method for a specific application.

Ion Exchange Process:

Basically the minerals present in water are in ionized condition. Ion exchange demineralization therefore is one of the most important and widely applied processes for the production of high-purity water for power plant services, and it is accomplished using resins that exchange one ion for another. Cation resins are solid spherical beads with fixed negatively charged sites and exchangeable positively charged sites. Anion resins are solid spherical beads that have fixed positively charged sites and exchangeable negatively charged sites. In their regenerated state for demineralization applications, cation resins are in the hydrogen form and anion resins are in the hydroxide form. The reactions of the resin beads with the dissolved impurities in the water are represented by the following:

Cation resin: $\quad R^-H^+ + C^+ \leftrightarrow R^-C^+ + H^+$

$\qquad\qquad\qquad 2R^-H^+ + C^{2+} \leftrightarrow R_2^-C^{2+} + 2H^+$

Anion resin: $\quad R^+OH^- + A^- \leftrightarrow R^+A^- + OH^-$

$\qquad\qquad\qquad 2R^+OH^- + A^{2-} \leftrightarrow R_2^+A^2 + 2OH^-$

where

R = resin matrix and fixed charge site;

C = cations such as Ca^{2+}, Mg^{2+}, and Na^+; and

A = anions such as HCO_3^-, Cl^-, and SO_4^{-2}

The hydrogen ions (H^+) displaced from the cation resin react with the hydroxide ions (OH^-) displaced form the anion resin. The net effect is the dissolved ions are removed from the water and replaced by pure water (H_2O).

The ion exchange resins are contained in ion exchange pressure vessels. The ion exchange resin in the vessels is referred to as the resin bed. This process of exchanging dissolved impurities is cyclic. When a resin bed site is exchanged with a dissolved ion, the site becomes "exhausted" and cannot remove other impurities without releasing an impurity. Exhausted resins must be regenerated to return the resin beads to the original hydrogen form for cations and hydroxide form for anions before further ion exchange can take place.

Cation resins are commonly regenerated with a strong acid solution of either sulfuric or hydrochloric acid. Sulfuric acid does not present the fuming problems associated with concentrated hydrochloric acid and is easier to handle (material selection). Consequently, sulfuric acid is frequently the recommended regenerant for cation resins. Anion resins are commonly regenerated with a sodium hydroxide solution. As can be seen from the regeneration reactions listed below, regeneration is the reverse reaction to the impurity exchange reactions.

Cation resin regeneration: $\quad 2R^-C^+ + H_2SO_4 \leftrightarrow 2R^-H + C_2^+SO_4^{2-}$

$\qquad\qquad\qquad\qquad\qquad R_2^-C^{2+} + H_2SO_4 \leftrightarrow 2R^-H^+ + C^{2+}SO_4^{2-}$
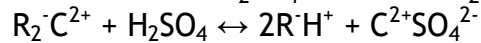
Anion resin regeneration: $\quad R^+A^- + NaOH \leftrightarrow R^+OH^- + Na^+A^-$

$\qquad\qquad\qquad\qquad\qquad R_2^+A^{2-} + 2NaOH \leftrightarrow 2R^+OH^- + Na_2^+A^{2-}$
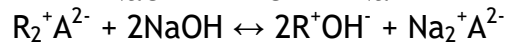
Ion Exchange Method:

Three primary methods are used to accomplish the ion exchange operation: fixed bed, fluidized bed and continuous bed.

With the fixed bed method, the inlet solution to be treated flows through the vessel. The ion exchange resin is not moved during the exhaustion; therefore, the resin remains a compact (unexpanded) bed or column during the service rum. Following exhaustion, the resins are regenerated.

With the fluidized bed method, the inlet solution to be treated flows upward in the vessel. The ion exchange resin bed is fluidized by the upward flow. The fluidized bed allows passage of suspended solids and results in less efficient contact. This process is used when suspended solids in the inlet solution are not removed. For high-purity cycle makeup treatment systems, the influent water is treated to ensure low suspended solids and fluidized beds are not employed.

This continuous bed method is similar to the fixed bed method in that the solution to be treated flows down and the resin bed is compacted. However, for the continuous method, a main vessel and a regenerative vessel are required. Small slugs of exhausted portions of the bed from the main vessel are removed to the regeneration vessel, and simultaneously, a slug of regenerated resin is returned to the main vessel. Although the resin slugs are transferred on an intermittent basis, the transfer is frequent and of short duration, so that the vessel service cycle is considered continuous. The continuous method is applicable for water treatment. However, compared to the fixed bed method, the continuous method is more complex, the capital costs for the control

system are higher, and the ion exchange resin is subject to greater attrition or wear and tear because of the frequent resin transfers. The fixed bed is predominantly selected as the preferred method of ion exchange, and the discussions that follow are based on the fixed bed method.

Ion Exchange Resins:
Cation resins are commercially available in strong-acid and weak-acid forms. Strong-acid cation resins can remove all cations in the influent water whereas weak-acid cation resins generally are restricted to the removal of hardness associated with carbonate alkalinity.

Anion resins are commercially available in strong-base and weak-base forms. Strong-base anion resins are capable of removing both weakly dissociated and strongly dissociated acids. Weak-base anion resins primarily provide removal of the strongly dissociated acids (such as hydrochloric, sulfuric, and nitric) and have only limited capability for removal of weakly dissociated acids.

Cation and anion resins have different affinities for the different dissolved ions. Consequently, the cation and anion resins display a selectivity series for dissolved ions. Listed below is a representative selectivity series for commonly used strong-acid cation resins and strong-base anion resins with the ion having the greatest affinity for the resin at the bottom of the list.

Selectivity of strong-acid cation and strong-base anion resins

Cations	Anions
Calcium (Ca^{2+})	Sulfate (SO_4^{2-})
Magnesium (Mg^{2+})	Chloride (Cl^-)
Ammonium (NH_4^+)	Bicarbonate (HCO_3^-)
Potassium (K^+)	Silica (exchanges as $HSiO_3^-$)
Sodium (Na^+)	Hydroxide (OH^-)
Hydrogen (H^+)	

The relative selectivity of the ions determines the exchange chemistry of the resin bed. Figure 15-10 represents a cation and anion resin bed during a service cycle. As seen in the "partially exhausted" resin bed, since the affinity of the cation resin for the calcium ion is greater than for the other cations shown, the upper layer of cation resin will be occupied predominantly by calcium ions. Since magnesium is next in the selectivity series, the layer of resin below the calcium layer will be occupied predominantly by sodium ions, for which the resin has the least affinity.

As the service run continues, the incoming calcium, which has the greatest affinity, replaces the first available magnesium-held site. The displaced magnesium and the incoming magnesium displace sodium-held sites. The sodium ions move farther down the resin bed and are exchanged by "approaching exhaustion" view, the band of each ion grows in depth during the service run in proportion to the relative concentration of the ion in the influent water. In the "exhausted" view, all of the available hydrogen exchange sites of the resin have been exchanged and the resin bed must be regenerated. At the point of exhaustion, ions, primarily sodium, break through into the effluent as

they are exchanged for an ion of higher affinity. This breakthrough of undesirable ions is called "leakages".

This same description of the service runs applies to the anion resin bed with the selectivity series determining the position of the layers of ions. Since bisilicate has the lowest affinity, it is the predominant ion to break through when an anion exchanger exhausts.

A wide variety of ion exchange resins have been designed, with different resin structures offering different advantages. For example, some resins have increased cross-linkage to improve resistance to oxidation and osmotic shock. Other resins have greater porosity to lessen irreversible organic fouling from waters containing organic materials. The type of resin selected must be determined based on the constituents in the water. Table 15-8 is a compilation of some of the resins available from various resin manufacturers illustrating differences in resin characteristics.

As a rule, water containing strong oxidizers, such as free chlorine, damages ion exchange resins. If these oxidizers are present in high concentrations, treatment is required to convert or remove the oxidizers prior to ion exchange.

The capacity of a resin is a rating of the ion removal capability of the resin and is reported in kilograins of ions per cubic foot (kilograms per cubic meter) of resin. The capacity that can be obtained from a resin is a function of the type of resin selected, the constituents in the influent water, the regenerant dosage [pounds of regenerant pr cubic foot (kilograms per cubic meter) of resin], and for anion resins, the temperature of the regenerant solution when silica is to be regenerated from the bed. The regenerant dosage rate is a function of the leakage rate that can be tolerated from the ion exchange bed. Each resin manufacturer has characteristics curves for each resin product used to determine resin capacity and regenerant dosages based on a specific water analysis. Many water treatment design engineers use proprietary procedures that incorporate additional factors into the resin rating process to more accurately reflect plant operating conditions and experiences. Operating experience has shown that use of these procedures often results in a more reliable long-term estimation of resin capacities, especially for some anion resins. However, the manufacturer's curves may be used to compare products and to develop preliminary design information.

Ion Exchange Equipment:

Ion exchange vessels are typically vertical cylindrical pressure vessels with either dished or elliptical heads. Ion exchanger vessels are constructed of carbon steel and are of welded construction.

The vessel interiors are lined for corrosion resistance. Several lining materials can be used, but natural rubber is frequently selected because of its long history of successful use. The internals for the ion exchange vessels are dependent on the design of the regeneration process. Except when hydrochloric acid is the regenerant, vessel internals of

316 stainless steel give good performance. Polyvinyl chloride (PVC) internals are also often supplied and have given satisfactory performance.

To prevent channeling and ensure uniform contact of the inlet water and the regenerant with the resin bed, the design and placement of the distributors in the vessel are critical. For in-place cocurrent regeneration, an inlet distributor, regenerant distributor, and underdrain system are required. If the vessel is a mixed bed exchanger, a regenerant interface collector is also required.
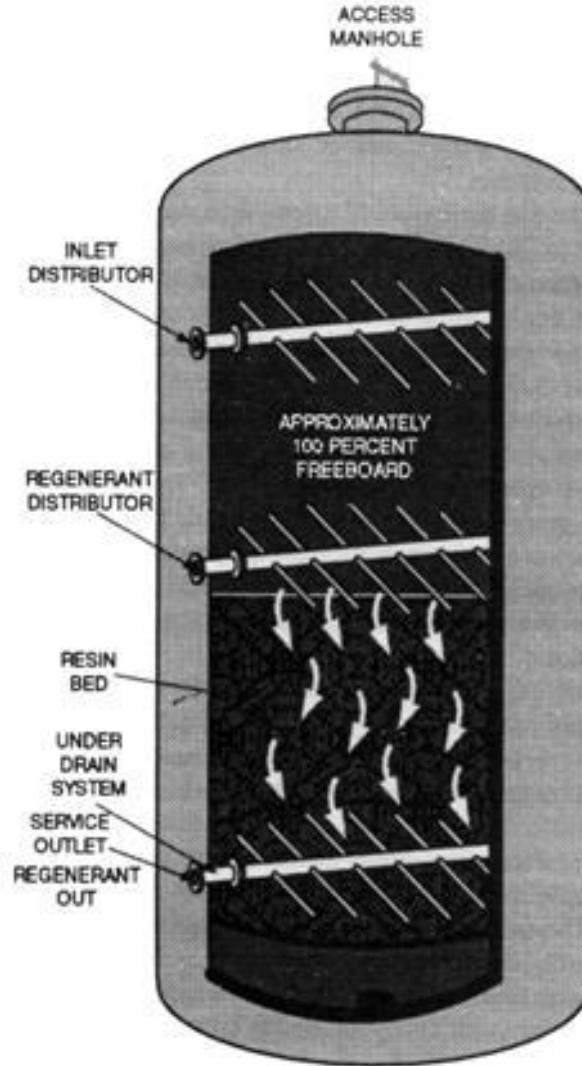

Fig. 4

Fig. 4 shows a typical cocurrent regenerated demineralizer exchanger vessel. The inlet distributor at the top of the exchanger evenly distributes the inlet flow in the service mode and collects the backwash flow and distributes the fast rinse flow in the regeneration mode. The regenerant distributor is located slightly above the resin bed and evenly distributes the regenerant solution and the slow rinse water during regenerant application. The underdrain system collects the treated water and collects the regenerant solution, show rinse water, and fast rinse water in the regeneration mode. For mixed bed exchangers, a regenerant interface collector is installed to collect the regenerant solution flows and the slow rinse flow instead of these flows being collected by the underdrain system.

For in-place countercurrent regeneration of downflow service demineralizer exchanger, an inlet distributor, regenerant collector, and an underdrain system are required. The inlet distributor is located at the top of the exchanger, evenly distributes the inlet flow in the service mode, and collects the backwash flow and distributes the fast rinse flow in the regeneration mode. The regenerant collector is just below the top of the resin bed and collects the regenerant solution and the slow rinse water, and distributes the partial backwash water in the regeneration mode. The underdrain system collects the treated water flow in the service mode and distributes the regenerant solution, the slow rinse water, and the full backwash water (when required) in the regeneration mode.

Back Wash:
Water is passed upwards in reverse flow through the column and then thrown to drain. This loosens and cleans the ion exchange material and prevents it from becoming packed. When the water enters at the bottom the whole bed is loosened and lifted up. The swollen bed height can be seen through a glass window. The top level of resin bed to which it has to raise is marked on the glass window. Quantity of back wash water is to be maintained such that the resin bed is always raised and held at that level marking through out the back wash process. During back wash air scoring is also given to loosen the impurities got accumulated in the bed.
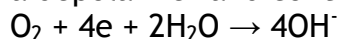
Acid wash:
The required amount of hydrochloric acid is injected into the units after diluting it to required concentration. Proportioning of 30% acid solution into 7% dilution is done through a water injector. When water flows through the injector it creates vacuum at the throat and the acid is sucked through line, which is connected to the throat. After the throat the acid and the water get mixed up thoroughly and the effluent is let out to sewer canal. Usually the sewer canal consists of a level mark. The acid water mix flow is always to be maintained to corresponding level mark during acid dosing. The acid effluent is taken to a neutralizing tank, where the solution can be mixed with required quantity of bleaching powder or lime soda so increase its PH to +8 and pumped out to sewage system.

Rinse:
Water is passed downwards through the column. This brings the regenerant into contact with the whole of the exhausted resin bed. The rinse is continued till excess regenerant has been removed.

Deaeration (Degasification):
Deaeration is the process of removing dissolved corrosive gases (O_2 and CO_2) from water. This process is also called degasification. Dissolved oxygen acts as a depolarizer and contributes to the corrosion of metal
$$O_2 + 4e + 2H_2O \rightarrow 4OH^-$$
Whereas Carbon dioxide dissolved in water liberates H^+ ions that attack metal
$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \text{ (carbonic acid)}$$
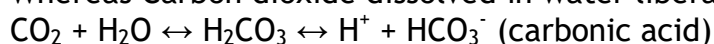
The process of deaeration is most frequently applied in boiler feed water heaters to protect piping, boilers and condensate equipment from corrosion. Deaeration is a thermal method where water is heated to bring about degasification, unlike de-oxygenation where it is carried out mainly by chemical techniques. The three cardinal principles that must be satisfied in any mechanical deaerator are:

Heating: Water must be heated to full saturation temperature (boiling point), corresponding to the steam pressure in the unit. Since, theoretically, the solubility of any gas is zero at the boiling point of the liquid, complete gas removal is not possible unless the liquid is kept at boiling temperature.

Mechanical agitation: The heated water must be mechanically agitated, by spraying, cascading over trays, or by atomisation, to expose maximum surface contact to the scrubbing atmosphere, thus permitting complete release and removal of gases.

Complete gas removal: adequate steam must be passed through the water to scrub out and carry away the gases after release. Extremely low partial gas pressure must be maintained since Henry's law states that the amount of gas which will dissolve in a liquid is proportional to the partial gas pressure in the atmosphere contacting the liquid. It is mandatory that the volume of scrubbing steam be high to produce the low partial gas pressure, and it is equally mandatory that the conditions prevail through out the deaeration process.

Thermal deaeration:
Upon heating water, the solubility of gases dissolved in it decreases because their partial pressure in the gas phase above the water level drop off.
So when water at a given pressure is heated to boiling point degasification is effected.
$x_{H2O} = n_{H2O}/\sum n$; $x_{O2}/\sum n$; $x_{CO2} = n_{CO2}/\sum n$
Now
$x_{H2O} + x_{O2} + x_{CO2} = 1$
Where x stands for the mole fraction of a component.
As the mole fraction of O_2 and CO_2 decreases in the vapour phase so does their partial pressure.
$PO_2 = x_{O2} \cdot$ (Total pressure)
$PCO_2 = x_{CO2} \cdot$ (Total pressure)
(Since the solubility of gases in a liquid is proportional to their partial pressure above the liquid phase, the decrease in the partial pressures of oxygen and carbon dioxide as a result of heating of water lowers the solubility of O_2 and CO_2 in water.)

Deaerator: A deaerator is the apparatus wherein deaeration is carried out. Deaerators are classified according to the working pressure under which they operate:

Type of Deaerator	Working Pressure
1. Vacuum Deaerator	0.116 MN/m^2
2. Atmospheric Deaerator	0.12-0.17 MN/m^2
3. High Pressure Deaerator	0.17-0.7 MN/m^2

Atmospheric deaerators can be subdivided into direct-contact (mixing) deaerators and overheated water deaerators.

Also deaerators can be classified in accordance with the mode of steam-water distribution in them.

1. Atomizing deaerator
2. Tray-type deaerator
3. Film-type deaerator.

A direct-contact deaerator consists of a deaerator column fitted on the top of the storage tank. The deaerator column is a hollow cylindrical vessel provided with

(a) Perforated, horizontal trays arranged one above the other.
(b) Water distribution device at the top.
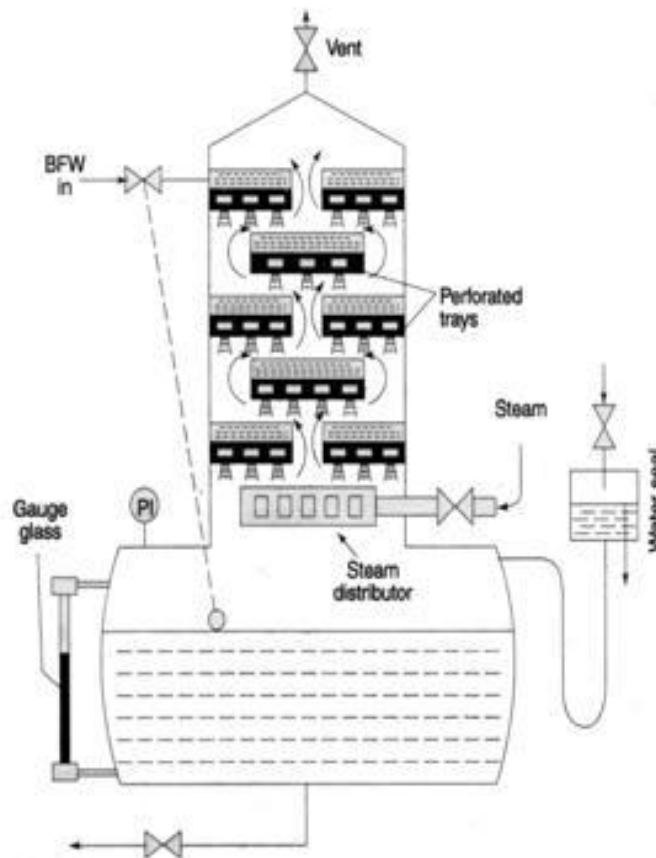(c) Steam distributor at the bottom. (Fig. 5)

Fig. 5

Feedwater enters the deaerator from the top and is evenly distributed, by means of the distributing device, into the perforated trays fitted at the bottom. Water fills the perforations (dia 5-7 mm) and rains down and comes in contact with heating steam dissolved into the lower portion of the deaerator column through the steam distributor. As a result of heat exchange between

the steam going up and the feedwater stream flowing down, the water gets heated up to its boiling point and the gases (O_2, CO_2) dissolved in it are transferred to the gas phase. These gases together with non-condensing vapour are vented into the atmosphere through a vent valve or pass into a vent condenser where the steam is condensed and the O_2 and CO_2 are vented.

The deaerated water is collected in the storage tank which is fitted with gauge glass, pressure gauge and hydraulic seal to avoid the formation of high pressure or vacuum in the deaerator.

Carbon dioxide can be removed by either vacuum degasification or forced draft degasification. A vacuum degasifier is a packed tower in which the water is sprayed and the gases are removed to a low level by maintaining a vacuum in the tower.
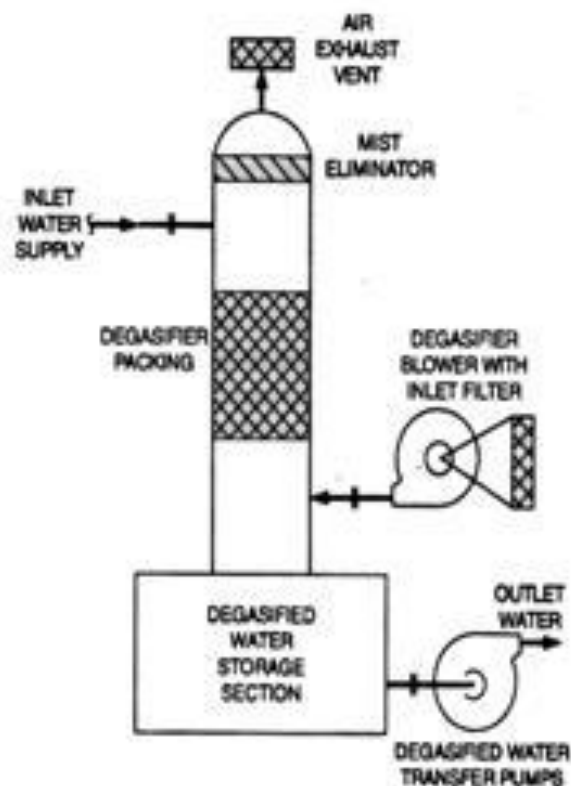

Fig. 6

Fig. 6 is a schematic representation of a typical two-stage vacuum degasifier. A forced draft degasifier is a packed tower in which the water is sprayed down the column and the carbon dioxide is removed by air that is blown up the column. A typical forced draft degasifier is shown schematically in Fig. 7.

Determination of whether a gasifier is to be used and the type of degasifier used depends on the amount of CO_2 produced following cation exchange and the effluent water quality (dissolved oxygen content) required. For moderate to large concentrations of carbon dioxide, it is more economical to remove the CO_2 by degasification than by anion exchange.
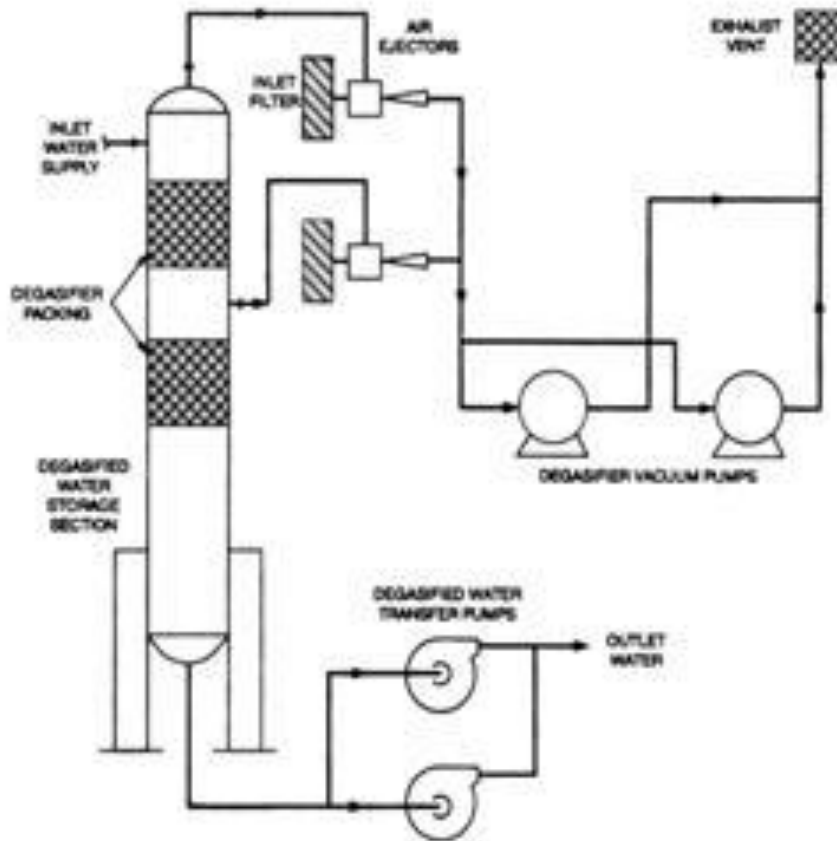
Fig. 7

Demineralized water storage:

Demineralized water is stored in tank. This is a cone-roof tank with a capacity which is adequate to meet normal plant requirements for 12 hours Tank accessories include level indicator, inlet level controller, inlet flow control valve and by-pass, drain, overflow, and piping. The inside of the tank is painted with vinyl paint. Pumps take suction from the Demineralized water storage tank and convey the water to the deaerating heater.

Mixed Bed:

The effluent water from anion exchanger may still have some silica. The water needs to be polished. Hence the water drawn from DM tank before it is supplied to boiler feed is passed through mixed bed exchanger. The mixed bed exchanger is similar to Cation or Anion exchangers. It consists of both Cation and Anion resins mixed together and filled up. Hence the DM storage water is flowing through the mixed bed resins the traces of all Cation and Anions are totally absorbed and removed.

The process of regeneration is similar to the regeneration process of Cation and anion exchangers. After back washing the Cation gets settled at the bottom and the anion resin at the top of the Cation bed. For regeneration the acid is

introduced at the middle and is taken out at the bottom. For anion regeneration the alkali is introduced at the top and drained from the middle.

Other Important Processes and Terminology Connected with Demineralization of Water:

Rinse:

An ion exchange resin bed should always be rinsed with water after flow of regenerant has ceased. Rinsing is a most important step and demands some consideration since this step actually concludes regeneration as it displaces the bulk of the regenerant solution from the resin bed. The rinse water also removes the products of regeneration together with the excess regenerant solution. At the conclusion of regeneration, most of the regeneration products are in the bottom portion of the exchanger, but at low concentration. These are removed with a small volume of rinse water. The regeneration solution, however, is at a high concentration throughout the vessel and reduced to a very low level before the next exhaustion cycle is started. After the initial rinse at regenerant displacement the flow rate is increased to remove the residual regeneration solution. Among the several physical, chemical and hydraulic characteristics of the ion exchange resins, the following ones present a particular interest.

Exchange capacity:

Exchange capacity is measured in grams of ions absorbed in the bed during the de-ionic process (expressed as calcium carbonate) per liter of resin quantity. The quantity of ions that can be removed from a solution by an ion exchange resin is equivalent to the exchange capacity of the particular resin. The exchange capacity is influenced by various factors like the regeneration procedure and the chemical composition and flow rate of the influent and effluent water.

Regeneration level:

Regeneration level is measured in grams of regenerant chemical (as 100% Hydrochloric Acid or Sodium Hydroxide) per litter of resin. The flow rate in the regeneration step is of critical importance, as it has a very marked effect on the capacities of the resin at all levels of regeneration.

Regeneration Efficiency:

The regeneration efficiency of resin is the ratio between the Exchange capacity and the Regeneration Level.

Ionic leakage:

Ionic leakage is revealed by the sudden increase in electrical conductivity of the effluent water is due to the impossibility to obtain a 100% theoretical ion exchange process. This is a complex phenomenon depending on many correlated factors.

Conductivity meter:

The purpose of the conductivity meter is for continuously controlling the Demineralized water effluent and signaling the exchange process exhaustion and consequent necessity to regenerate the exhausted train.

Due to the extremely low salinity content of Demineralized water it would be impractical to measure it gravimetrically. For this reason the more accurate and immediate electrical conductivity measure of the Demineralized water is used, by taking advantage of the capability of ions to conduct electric current in an aqueous solution. The higher the salinity, the number of ions present the higher will be the electrical conductivity. Under present circumstances 1 ppm of residual salinity corresponds to an electrical conductivity of 5 micro-Siemens (at 20˚C), thus giving a measure of operational leakage from the Demineralized trains (normally ranging around 10 micro-Siemens or 2 ppm residual salinity consisting of NaOH traces). When a stage of the Demineralized train is exhausted the effluent salinity will rapidly increase and be signaled by a corresponding increase in conductivity. As a general rule, under normally experienced conditions, a sharp increase in the effluent conductivity is also matched by an increase (a marked increase) in the silica content of the effluent. For this reason and to avoid over exhaustion of the resins it is strongly recommended to regenerate the train as soon as a sharp increase in conductivity is experienced (conductivity higher than 3 to 5 micro-Siemens). Slight fluctuations in the recorded conductivity of effluent might be experienced without any special significance on the train operation, being due to slight fluctuations in filtered water quality or rate of changes through the train.

Membrane Desalination Process (Reverse osmosis):

Reverse osmosis is a pressure driven membrane process capable of removing small particles, dissolved in salts and low molecular weight organics from a feedwater stream. If two aqueous solutions containing differential salt contents are kept separated by a semipermeable membrane, the system develops an inherent tendency for water molecules (not the salt) to permeate across the membrane layer to dilute the more concentrated solution. This process is called osmosis. The driving force per unit membrane cross-section, dependent on the concentration difference, is the osmotic pressure.
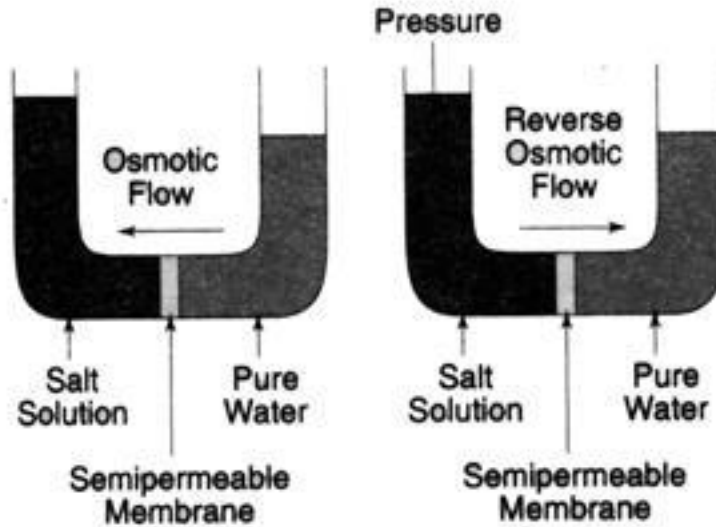
Fig. 8

However, this natural process can be reversed if some external pressure higher than the system's osmotic pressure is applied on the concentrated solution side whereupon water will pass from the more concentrated solution, through the membrane boundary, to the less concentrated solution. This is the basis of reverse osmosis. (Fig. 8)

If one compartment contains pure water and the other salt or mineral-rich water, the process of reverse flow will produce pure water, since the membrane is not permeable to salt.

The RO processes are classified by their cross-sectional morphology as

(a) asymmetric

(b) thin-film composite.

The RO process cannot go on indefinitely. The salt solution would require increasingly higher pressure to force water through the membrane; ultimately the membrane could become clogged by precipitated salts and other impurities. In actual practice, RO devices employ crossflow filtration as shown in Fig. 9.
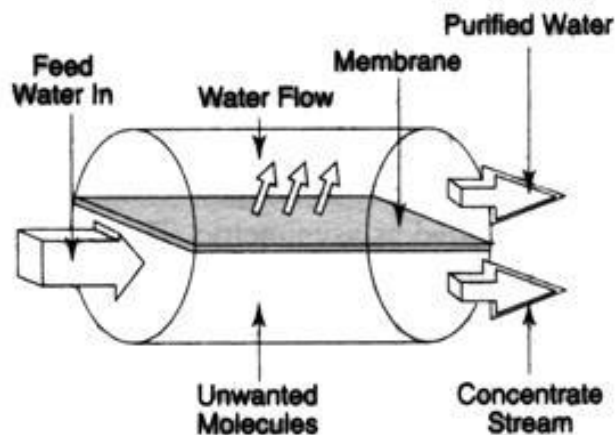

Fig. 9

This method uses a pressurized feed stream which flows parallel to the membrane surface. Only a portion of this feed stream passes through the membrane as permeate and the remainder of the stream known as the reject or concentrate provides a continuous sweep of rejected ions and particles from the membrane surface.

Thermal Desalination Process:

It is based on using heat to vaporize a portion of the fluid (brackish water or sea water) treated. The vapour is subsequently condensed as pure water. Basically, there are three commercially available technologies by which thermal desalination can be accomplished:

- Multiple effect distillation
- Multistage flash evaporation
- Vapour compression

The thermodynamic principles of operation for the processes are same; the processes vary in method and operating conditions used to accomplish the desalination.

Demineralizer Plant Effluent (Waste Water) Treating Unit:

All the waste water from different units are taken into the equalizing basin water inlet channel. The acid wastes are neutralized by lime injections:

$$2HCL + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$$

The plant consists of an equalizing basin divided into two compartments from where part of the waste water is pumped into the Flash Mixer by means of waste transfer pumps and the other part goes back into the equalizing basin. The purpose of dosing this is to get a homogeneous mixture of the waste effluent in the equalizing basin, which would enable the lime dosing to be even and consistent. The lime injected into the waste line at the discharge of the waste transfer pump before the waste enters the flash mixer. The lime dosing is done in conjunction with the PH value of the effluent entering the flash mixer. PH value is recorded by the PH meter located on the inlet line of waste effluent to the flash mixer. Waste water collects in the equalizing basin. Waste water is pumped to the flash mixer by centrifugal type waste water pumps, suitable for handling an acidic effluent. The pumps are complete with electric motors, valves and accessories. Ahead of the flash mixer lime is blended in line into the waste stream to adjust the PH of the waste water before it is routed to the sewer.

The neutralized waste effluent will have a pH value of not less than 6.5 at 20`C. Lime is prepared at start-up and is dosed following the indications of the pH meter.

Chemical conditioning of Boiler water:

Demineralization of water renders raw water fit for use as make up and feed to a boiler. Just feeding a boiler with Demineraliser water, which is free of all impurities, alone, will not suffice in reality due to the following reasons.

a) When the steam is continuously being generated and released for process, the water inside the drum gets more and more concentrated, even with the very little and negligible level of impurity in feed water.

b) Further the pH of Demineralized water normally remains to be close to neutral and will induce low pH corrosion of tube and pipe materials.

c) Demineralized water when under storage absorbs atmospheric air and the level of dissolved Oxygen in water increases. Presence of Oxygen in feed water again renders it corrosive.

Hence it is essential and pertinent to further chemically treat the demineralised water, which is taken as make up feed to boiler. Chemical treatment is done at various stages for feed and boiled water, steam and return condensate, in order to ensure adequate protection is established over the entire system, to help prevention of direct attack on parent metal by the corrosive elements present in water / steam cycle.

The chemical treatment technique is based on several factors. While the overall conditioning concept remains the same, there would be variations in the methods adopted and the residual levels optimized, it depends mainly on:

a) Deferent grades of ferrous and alloy metals which are deployed in the design and manufacturing of various pressure part components, such as, water wall tubes, headers, raiser tubes, economizers, super heaters, reheaters etc. and so many other equipment down the line such as turbines, condensers, various stages of regenerative system heaters and the pumps,

b) Working temperature and pressure at which the steam is generated for supply to end users,

c) The type of fuel used and the firing system adopted,

d) Release of heat flux density, depending on the fuel fired and the design and size of the furnace,

e) Capacity of boiler for steam generation and the level of steam purity expected,

f) Quality and quantity of condensate recirculated within the system.

The condensate extracted from the Condenser is passed through a Dearetor to get rid of dissolved oxygen, by mechanical stripping action. The feed water is then chemically conditioned further with dosing of chemicals to ensure that the dissolved oxygen content of the water is reduced to the minimum. Hydrazine hydrate is normally employed for this purpose. A lean solution of Trisodium phosphate in water is dosed into the drum directly for buffering and maintaining boiler water with a required level of alkalinity. The process does not end here. Various other problems could be encountered during operation. Norms and recommendations are prescribed for guiding conditioning technique. Conditioning techniques and details have also been discussed in the section dealing with recommendations and the comments arising from them.

We will learn about boiler water internal treatment process and its needs and effects in detail in the following.

Chemical Treatment of Water in Steam Generating Systems:

Introduction:

The inhibition of corrosion in steam generators and auxiliary equipment during operation is essential, for preventing damage to tube material and innumerous hazards caused, generally resulting in equipment damage. Due to such damages, repairs and maintenance expenditure increases demanding costly replacement of spare parts, in addition to unwanted downtime, with corresponding loss of production. The iron and copper corrosion products, from preboiler system, are often carried away into the boiler and cause harmful scale deposits, contributing to caustic or hydrogen attack, as dictated by conditions within the system.

Oxygen pitting - causes and remedy:

The presence of dissolved oxygen in boiler system water causes the cathode of any corrosion cell to depolarize, thereby sustaining the corrosion process. The most familiar form of oxygen attack in boilers and steam and condensate systems is pitting.

The presence of oxygen is also a necessary component of other corrosion mechanisms; however, its role is less obvious. Dissolved oxygen is essential to ammonia corrosion of copper alloy condenser tubes and contributes to chloride-induced stress corrosion cracking of austenitic stainless steels in steam generators. It is, therefore, essential that the dissolved oxygen concentration be kept at the lowest feasible and economically justifiable level throughout all steam generating systems regardless of type, size or pressure. This requirement grows more critical as the operating pressure increases and as systems become larger, because the cost and danger of equipment failure increase proportionately.

In larger and more complex systems, the major portion of dissolved oxygen can be removed mechanically by such devices as deaerating feedwater heaters, condensers or hot process softeners. It is important to note that mechanical deaeration must be applied not only to the makeup water stream but also to any return condensate, especially if the condensate return system operates under a vacuum, or if the condensate receivers are vented to the atmosphere.

Under optimum operating conditions, it is often impossible for mechanical deaerators to reduce the dissolved oxygen level below 0.005 cc/l or 0.007 ppm. Any deterioration in Dearetor performance will result in increase of dissolved oxygen in feed water. The usual practice is to resort to addition of chemical reducing agents to scavenge any residual oxygen present in water.

Oxygen scavengers:

Feed water treatment with Sodium Sulfite (Na_2SO_3):

Sodium sulfite has long been used as an oxygen scavenger in boiler feed water treatment. It reacts readily with oxygen, particularly at elevated pH and temperature, to form sodium sulfate by the following reaction:

$2\ Na_2SO_3 + O_2 \rightarrow 2\ Na_2SO_3$
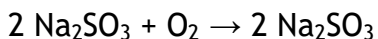
This reaction reveals that 7.88 parts of pure sodium sulfite – or about 8.5 parts of commercial grade 93% Na_2SO_3 – will scavenge one part of dissolved oxygen. A residual of 30-50 ppm as SO_3 is usually maintained in boiler water at pressures below 600 psig to provide impetus for the chemical reaction.

When any oxygen scavenger is used, it is essential to ensure total chemical deaeration before the feedwater reaches the boiler. Especially it is essential to ensure this aspect, while using sulfite, since oxygen remaining in the feedwater when it reaches the boiler will flash into the steam phase, whereas the sulfite will remain in the water phase since it is nonvolatile.

It is advisable to dose sodium sulfite to the condensate water or at the feed water storage tank to ensure complete chemical deaeration in the preboiler section, so that it is possible to allow sufficient reaction time for deaeration.

The reaction rate of sodium sulfite with oxygen is proportional to the concentration of both sulfite and oxygen and to the temperature and pH of the feedwater. To ensure complete oxygen removal when one of these factors is unfavourable, or when the retention time allowed for the reason is short, a catalyst is often added to the sodium sulfite to increase its reaction rate. Cobalt salts are the most commonly used materials to catalyze the reaction.

Although the use of sulfite is common in plants with low and moderate pressure boilers, it is usually avoided in higher pressure boilers. Susceptibility to carryover, caused by the over concentration of dissolved solids in boiler drum, generally increases with pressure and may subsequently increase the demand for blow down in high pressure boilers. This is especially true for boilers using demineralized makeup water, in which a significant percentage of dissolved solids in the water will result from the use of sodium sulfite.

The use of sodium sulfite should also be avoided in high pressure boilers because of its potential for thermal decomposition according to the reactions:

$Na_2SO_3 + H_2O + Heat$

$2NaOH + SO_2$

$4Na_2SO_3 + 2H_2O + Heat$

$3Na_2SO_4 + 2NaOH + H_2S$
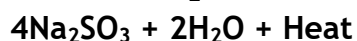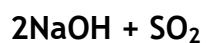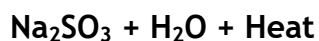
These reactions have been shown to take place at boiler pressures as low as 40 kg/sq cm, although they do not usually create a serious problem until pressures exceed 60 kg/sq cm Because these reactions are determined by a combination of the sulfite concentration, the boiler water chemistry and the boiler design, the interrelationship of these factors at an individual plant will govern the extent to which they are a problem. The main problem associated with sulfite breakdown is the formation of SO_2 and H_2S which can cause corrosion in the after-boiler sections when they condense to form acids. In steam systems where there are turbines, any SO_2 generated by sulfite breakdown will dissolve in the first fraction of condensate formed, which is typically at the back end of the turbine. The low pH solution of sulfurous acid created can rapidly attack turbine blades. This acid attack can even occur with steam whose pH has been raised by treatment with an amine. The distribution ratio for the amine may be much higher than that for SO_2; therefore, it will not condense in the turbine

area to elevate the pH. In high pressure boilers utilizing a coordinated phosphate-pH treatment, the use of sodium sulfite is undesirable because the introduction of sodium ions to the feedwater will alter the balance of sodium to phosphate being maintained in the boiler.

Feed water treatment with Hydrazine (N_2H_4):

The widely used chemical oxygen scavengers in high pressure boiler operations is hydrazine (N_2H_4). The advent of an organically catalyzed hydrazine suitable for use in boilers made the full benefits of hydrazine available to low and medium pressure applications and more extensive in high pressure systems.
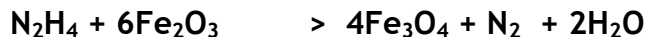
The reaction of hydrazine with oxygen is as follows:

$N_2H_4 + O_2 \quad > \quad 2H_2O + N_2$

It is important to note that the products of the hydrazine reaction are inert and volatile. They will, therefore, not add any dissolved solids in the boiler water.

Hydrazine will also react with:

Ferric oxide

$N_2H_4 + 6Fe_2O_3 \quad > \quad 4Fe_3O_4 + N_2 + 2H_2O$

and Cupric oxide:

$N_2H_4 + 4CuO \quad > \quad 2Cu_2O + N_2 + 2H_2O$

Magnetite, Fe_3O_4, and cuprous oxide, Cu_2O, are the passivated oxide states of iron and copper. Hydrazine, therefore, renders iron and copper surfaces less susceptible to corrosion by reducing them to a passive state. The reduction reactions take place on metal surfaces in the pre-boiler, the boiler and the after-boiler, as well as on suspended ferric oxide or cupric oxide. Hydrazine is fed in amounts required to react with dissolved oxygen, ferric ions, and cupric ions, plus a small excess. The theoretical requirements for pure N_2H_4 are 1 ppm per ppm O_2, 0.048 ppm per ppm Fe^{+3}, and 0.125 ppm per ppm Cu^{+2}. Initially the use of hydrazine was most extensive in high pressure boilers in which sulfite would cause problems (as previously discussed). Hydrazine's relatively sluggish reaction with oxygen prevented its use in low pressure boilers. In high pressure systems, the temperature of the boiler feedwater is usually sufficient to permit the effective use of hydrazine. An organic catalyst was then developed which increased the reaction rate of hydrazine with oxygen, permitting its effective use in boilers utilizing lower temperature feed water. The increased reaction rate with catalyzed hydrazine brought the added benefit of metal passivation and low temperature condensate protection to both high and low pressure systems, even when a catalyst was not necessary for effective feedwater oxygen scavenging. The basic reactions of catalyzed or uncatalyzed hydrazine are identical except that in the case of the catalyzed version, reactions occur 10-100 times faster.

Effect of temperature on Hydrazine:

In steam generating systems operating above 0.5 Kg/sq cm (110°C), hydrazine volatizes from the boiler along with the steam. The degree of volatilization is

proportional to the temperature of the boiler water. Therefore, the water temperature dictates the maximum attainable hydrazine concentration in the boiler water. Between 110°C and 270°C, hydrazine volatilization increases, but only slight hydrazine breakdown occurs. At 270°C, hydrazine undergoes rapid thermal degradation:

$3N_2H_4$ + Heat N_2 + $4NH_3$

This reaction occurs relatively slowly at low levels of hydrazine but becomes more rapid as the hydrazine level increases. The above reaction must be considered carefully when hydrazine is used in systems where the boiler water or superheated steam temperature is above 270°C and copper is used in the after-boiler section, because in the presence of oxygen, ammonia can attack copper alloys. It is the reason Hydrozin dosing is invariably done either at condensate line or at feed water suction line where the temperature is well below 270°C

Control on dosage of Hydrazine:

A hydrazine residual of 0.1-0.3 ppm is usually maintained in the boiler water in boilers operating at less than 600 psig. Above that pressure, the residual is most commonly controlled at 0.05-0.1 ppm. The extremely low hydrazine residual in the boiler, as well as the inert nature of the products of the hydrazine reaction (N_2 and H_2O), make its use extremely desirable in systems in which total dissolved solids in the boiler water constitute the limiting factor for boiler blow down. In such systems, the substitution of hydrazine for sulfite can permit increased cycles of concentration. In some systems, the hydrazine level is controlled in the feedwater rather than in the boiler water. This is done to assure that a hydrazine driving force exists in the feedwater and to minimize overfeed. When hydrazine is controlled in the boiler feedwater, a residual of 0.01 to 0.1 ppm is usually maintained. Because of hydrazine's volatility, it is not cycled to high concentrations in the boiler even when a relatively high feedwater residual is maintained and the cycles of concentration based on feedwater are high. Although a hydrazine residual is usually controlled in the boiler water or feedwater, control is done occasionally in the condensate return, or in a particular area of the after-boiler system. The selection of a site for control is dependent upon the hydrazine feed point and the location of the problem to be corrected.

Hydrazine should be fed to the boiler, pre-boiler or after-boiler section as dictated by the needs of the particular system and the problems to be solved. In systems where hydrazine must be fed directly to the boiler, control should be in the boiler water with periodic checks on the feedwater to insure pre-boiler protection. If fed to the storage section of deaerating equipment, hydrazine should be controlled in the feedwater just before the boiler, in the boiler water itself, or in the condensate. In systems where hydrazine is fed to the after-boiler, the preferred control point is in the feedwater, but control may also be at the boiler. In any case, the most desirable situation in terms of corrosion control is one in which hydrazine is found throughout all elements of the steam generating system: the pre-boiler, the boiler, and the after-boiler.

Safety in handling of Hydrazine:

Because pure hydrazine has a very low flash point and is a potential fire hazard. Hence Hydrazine is only used as a 15% or 35% aqueous solution. The Occupational Safety and Health Administration (OSHA) list Hydrazine listed as an animal carcinogen by the National Toxicology Program. Occupational exposure limit for hydrazine in workplace is air of 0.03 ppm as a ceiling concentration for any 2-hour period.

Carryover of Boiler Water – Priming and Foaming in boiler:

Mechanical entrainment is primarily a function of the design of the steam separators and method of operation of the boiler. It can be aggravated chemically by conditions, which produce foaming and thereby substantially increase the amount of droplets formed and their entrance into steam separating equipment. The entrainment process may be divided into two categories. One is being priming and the other foaming.

Priming:

Priming usually results from a sudden reduction in boiler pressure caused by a rapid increase in the boiler steam load. This causes steam bubbles to form throughout the mass of water in the boiler. Increased water volume raises the level in the drum, flooding separators or dry pipe. Priming may also result form an excessively high water level following a rapid load reduction caused by control failure.

Foaming:

Foaming is the buildup of bubbles on the water surface in the steam drum. This reduces the steam release space and, by various mechanisms, causes mechanical entrainment. Mechanical entrainment is usually controlled through proper design and subsequent efficient operation, supplemented by the use of antifoam agents when foaming becomes a problem.

Phosphate dosing and Corrosion in water tubes:

Water can enter the most nonporous of deposits on internal surface of the water wall tubes. The water entrapped inside the deposit layer gets maximum heat absorption and starts boiling. The ability of the main bulk of liquid to rinse the area at which the steam bubbles form is, therefore, impaired, resulting in further concentration of solids. If the boiler water composition is such that it becomes either strongly acidic or strongly basic as it concentrates, under-deposit corrosion will usually occur.

While resorting the traditional high phosphate levels of 20 to 40 ppm, to make the situation worse, simultaneously condenser tube leak also occurs, basic magnesium phosphate deposits take place, rather than the desirable and less adherent basic magnesium silicate (serpentine) or magnesium hydroxide (brucite). Hence in modern high pressure boilers in order to prevent this type of magnesium deposition, the concentration level of phosphate is reduced to 2
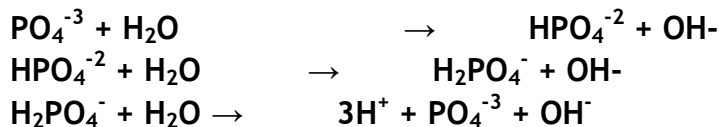
to 4 ppm of orthophosphate and the hydrate alkalinity to 15 to 50 ppm as $CaCO_3$. As operating pressure increase, waterwall tubes exposed to high density of heat flux. It has been observed that although deposits are controlled, failures do occur at times by metal losses characterized by large pits and grooves develop.
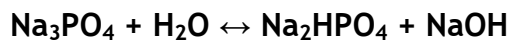
Coordinated Phosphate-pH Control

This system, which is called coordinated phosphate-pH control, depends on the feed of mixtures of orthophosphate or a mixture of caustic and disodium phosphate to control pH in an otherwise unbuffered water. Monosodium, disodium, and trisodium phosphates can accomplish this purpose as a result of their ability to hydrolyze to H_2PO_4 -, HPO_4^{-2} and PO_4^{-3} and to establish an equilibrium among these forms, in conjunction with OH-concentration or, by inference, the pH.

The reactions of concern are as follows:

$PO_4^{-3} + H_2O \rightarrow HPO_4^{-2}$ + OH-

$HPO_4^{-2} + H_2O \rightarrow H_2PO_4^{-}$ + OH-

$H_2PO_4^{-} + H_2O \rightarrow 3H^{+} + PO_4^{-3} + OH^{-}$

In water containing a low concentration of dissolved solids other than sodium phosphate, the equilibrium between various forms of phosphate ion can be utilized to control the acidity or alkalinity of the whole system. The ratio of one phosphate to the other can be controlled to produce any desired sodium to phosphate (Na/PO_4) ratio. If all of the phosphate is present in the trisodium form, the Na/PO_4 ratio is obviously 3.0. At or just below this level there will be no free hydroxide present. The total free sodium hydroxide or free caustic defines the amount of sodium hydroxide in solution in excess of that derived from the hydrolysis of trisodium phosphate according to the following equation:

$Na_3PO_4 + H_2O \leftrightarrow Na_2HPO_4 + NaOH$

The pH range for coordinated phosphate control should be 10.0 to 10.6. This corresponds to an orthophosphate residual in the range of 15 to 50 ppm. The molar ratio of sodium phosphate in the boiler water should be less than 3.0:1. Today, coordinated phosphate control programs maintain a 2.8:1 Na/PO_4 ratio. The phosphate residual is generally controlled between 5 and 10 ppm as PO_4 and the pH between 9.6 and 9.9. The upper limit on operating pressure for this program is regarded as 100 kg/sq.cm

Congruent control

As a result of the concentrating effect at the tube surface, it appears that a combination of trisodium and disodium phosphate precipitates form. If the sodium-to-phosphate ratio in the water phase is greater than that in the precipitate, the result is an excess of sodium hydroxide in the supernatant liquid. If the water phase and precipitate have the same ratio, they are chemically congruent. Further, if the ratio is congruent or lower in the water phase than in the solid phase, no free caustic can exist. The exact composition of the phosphate precipitate depends on temperature and has been found to be in the range of 2.6 to 2.8 for pressures ranging from 100 to 200 kg/sq.cm. Thus, a Na/PO_4 ratio of 2.6:1 is considered safe for all drum-type boilers.

The temporary deposition of usually water-soluble chemicals during normal operation is referred to as hideout. When the steaming rate is appreciably reduced, or the boiler taken off line, the deposited chemicals redissolve in the boiler water. Although a number of substances exhibit this phenomenon, sodium phosphate is of most interest in boiler operation. At temperatures above 110°C, Trisodium phosphate exhibits a retrograde solubility. It is this property that makes hideout possible. Phosphate hideout is also undesirable because it may raise tube wall temperatures and cause failures similar to those brought about by other deposits. Phosphate precipitation and the formation of free caustic can also occur if boiler water is totally evaporated in the steam blanketed area or is highly concentrated within or under a porous surface deposit.

Congruent control, used when phosphate hideout may occur, is similar to coordinate phosphate-pH control, except that the Na/PO_4 ratio is intentionally controlled at a specific value, usually 2.6 to 2.8. The concept of maintaining a specific ratio at 2.6 assures that no concentrated caustic solution can be formed in the event of phosphate precipitation. In this situation, the sodium and phosphate will invariably leave the solution in such proportions that the remaining solution has a Na/PO_4 ratio equal to original ratio, therefore without free hydroxide or caustic.

Volatile treatment

A review of high pressure boiler water treatment would not be complete without looking at the alternative to phosphate programs. This program uses all-volatile treatment chemicals and is commonly referred to as AVT or zero solids treatment. Sodium is eliminated from the feedwater by evaporation and/or demineralization of the makeup water and full flow, mixed bed demineralization of return condensate. No chemicals containing sodium are added for internal treatment. The chemicals used are all volatile materials are ammonia and/or morpholine or cyclohexylamine for pH control, and hydrazine, catalyzed hydrazine or a volatile hydrazine substitute as an oxygen scavenger and corrosion inhibitor. The control limits for an AVT program are total solids less than 2 ppm and a pH range of 8.5 to 9.0. Such treatment is limited to very high pressure boilers, usually in steam-electric generating systems. It is the only treatment system possible for once-through or monotube boilers, and most manufacturers of PWR-type nuclear reactors favor its use in the secondary steam generating loop to overcome unique crevice corrosion problems. It is occasionally employed in drum-type boilers operating at 200 kg/sq.cm and above but provides less safety and corrosion resistance against a temporary disturbance, particularly that of a condenser leak, than does the phosphate-pH treatment system. In actual operation, most systems using volatile chemistry provide a phosphate feeding facility for emergency use during a period when feedwater is contaminated with dissolved salts.

As pressures increase, film boiling and other causes of local overheating are most prevalent. This has led to the phenomenon known as caustic corrosion. Overconcentration of sodium hydroxide destroys the protective magnetic iron oxide film (magnetite-Fe_3O_4), and the base metal is then attacked by the concentrated sodium hydroxide as shown in the following two equations:

$$4NaOH + Fe_3O_4 \rightarrow Na_2FeO_2 + 2NaFeO_2 + 2H_2O$$
$$2\,NaOH + Fe^0 \rightarrow Na_2FeO_2 + 2H^0$$
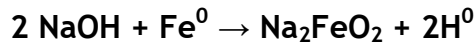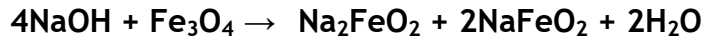
Caustic corrosion manifests itself as gouging and is fairly easy to identify. The tube does not lose ductility and, unless arrested, the gouging proceeds until thinning eventually causes tube failure.

It is generally accepted that caustic concentration in excess of 50,000 ppm or 5% is necessary for the above reactions to occur. While there is never caustic present to these levels in the bulk boiler water when using precision control, the concentrating mechanism at the tube surfaces that can occur above 900 psig limits its use to lower pressures.

The maintenance of clean boiler metal surfaces is a prerequisite for the prevention of caustic attack. Feedwater hardness, iron and copper should be kept at sufficiently low levels. Under ideal conditions, feedwater should contain no hardness, although this is not always possible as a result of inadequate performance of primary water treating equipment, condenser leakage, or other types of steam and condensate contamination.

Frequently, for boilers operating above 600 psig, the primary constituents in boiler deposits are metal oxides. Therefore, it is essential to maintain adequate control over preboiler and afterboiler corrosion. In addition, the use of condensate polishers may be desirable. Precommision cleaning of high pressure boilers is critical. It is essential that every tube and the associated feedwater and condensate systems be thoroughly cleaned. The presence of tramp iron, copper and silica can cause deposits and corrosion on startup.

Recommended Quality Parameters of Treated Water at Different Stages of Treatment:

Chemical treatment methods and recommendations:

Treatment methods and recommendations are prescribed to ensure the right type of treatment and conditioning technique. In practice, it has been established that if the recommended norms are maintained and proper control is exercised based on feed back analytical details, the system, as a whole would be free from problems. To keep the entire system sound and reliable, proper operation and maintenance care is additionally important. The desired results may not be necessarily achieved if the standards are not practiced in true sense. The standards prescribed give only the range within which it is safe to operate. The most adequate values have to be established within the framework prescribed, based on the type of boilers, the operating parameters, the manner of operation and essentially the feed back obtained from time to time.

Clarified and filtered water (inflow to D.M. Plant):

We have seen in section 1.6 above what is meant by process of clarification and filtering. The input to Demineralization plant must be clarified and filtered.

The water inflow to D.M. plant should be clear, colorless and odorless. It should be free from organic matters, free from chlorine and other oxidizing agents. Presence of oxidizing agents, organic matters etc. will affect the resin exchanging capacity and lead to total collapse of the resin by way of decrosslinking. It should be free from iron, which leads to resin surface contamination. PH control is equally important for maintaining raw water quality. A preferable range would be 7 to 9.0.

Strongly acidic Cation effluent:

The quality of effluent water of strongly acidic cation exchanger will have the following property:

PH at 25 °C	2.8 to 3.5
Free mineral acidity ppm as CaCO3 (FMA) [HCl + H2SO4 + HNO3 + H3PO4] = [Cl + SO4 + NO3 + PO4]	Should be equal to the total equivalent mineral acidity (EMA)
Hardness (Ca + Mg) ppm as CaCO3	NIL
Sodium ppm as Na+	< 0.005

Degasifier effluent :

Residual free CO2 ppm	< 5.0

Strongly basic anion effluent:

The quality of effluent water of strong base anion exchanger will have the following property:

pH at 25 °C	7.5 to 9.0
Hardness (Ca + Mg) ppm as Ca CO3	NIL
Total silica SIO2 ppm	Less than 0.05
Electrical conductivity MICROMHOS/Cm at 25 °C	< 2.0 preferably < 1.0
Chloride (ppm as Cl)	NIL
Organic matter (mg of KMn O4/Litre)	Practically free

There may be little consumption of KMnO4. It will be worthwhile to strive for a figure. of less than 1.0 ppm. While estimating, blank comparison is very essential.

Mixed bed effluent:

The quality of effluent water of mixed bed exchanger will have the following property:

pH at 25 °C	6.8 to 7.2 PH less than 6.8 is an indication of leakage

	of acidic sulphate and chloride salts and organic acids. D.M. plant performance needs checking up.
Electrical conductivity micromhos/cm at 25 °C through closed cell provision without any access to the atmosphere	< 0.2 micro seimensper sq.cm
Total hardness (Ca + Mg) ppm CaCO3	NIL
Total silica ; (SiO_2 ppm :)	< 0.02 (< 0.01 is preferable)
Chloride (ppm as NaCl) (By selective ion electrode)	NIL
Sodium (ppm as Na)	< 0.003
Organic matter mg of KmnO4/Litre	Should be practically free : There may be slight consumption of permanganate. It should be < 0.5 at any stage. < 0.2 is preferable. Blank comparison is essential. For blank test use reagent grade water.
General appearance	Clear, free from odour, colour and haziness. No glittering to tyndal effect.

Condensate and Return condensate:

The quality of condensate depends upon the quality and the quantitative addition of make up water. It is, hence, imperative to control CBD in order to limit make up consumption. If auxiliary steam for various purposes is consumed, this will boost the make up consumption. Under such circumstances, quality of make up should be closely monitored to achieve the recommended values, so that, the quality of extracted condensate is maintained. These recommendations are relevant for samples collected at the condensate extraction pump delivery, prior to hydrazine (L.P.) dosing point.

Quality of extracted condensate water:

pH at 25 °C	8.5 to 8.8
Electrical conductivity Micro mhos/Cm at 25 °C	< 0.3 (with correction for ammonia and hydrazine through strong cation column alone would ensure the desired purity.)
Dissolved oxygen (O2 ppm)	< 0.02
Dissolved carbon dioxide (CO2 ppm)	NIL
Total iron (Fe ppm)	< 0.01

Total copper (Cu ppm)	< 0.003
Total silica : (SiO ppm)	< 0.01
Total hardness (Ca + Mg) ppm as CaCO3	NIL
Sodium + potassium ppm	< 0.01
Free ammonia : ppm	< 1.0 (< 0.5 is preferable)

In order to get a reliable Conductivity and PH measurement the sample is to be cooled to 25 °C with continuous flow of sample flowing with a closed cell provision having no contact with atmosphere. The sample has to be passed through a strong acidic cation column to avoid the influence of dissolved Ammonia and Hydrazine.

In case carbon dioxide is present in condensate water, the conductivity measured even after passing through cation column will be indicated high, which will be proportional to the concentration of carbon dioxide in the sample. Sample should flow at a regular and constant rate and should be clear and colourless.

Drum sample quality is mainly dependent on the quality of the condensate extraction and make up water. Feed flow requirement is decided by leakages and is dependent on the drum operating pressure too.

Quality of feed water to boiler

Quality requirement for feed water is very much dependent on drum operating pressure. Hence recommended feed water quality is always expressed for a particular range of boiler operating pressure.

Drum operating Pressure Kg/Cm2	60	80	100	120	130 & above
pH at 25 °C	8.5~9.0	8.5 ~ 9.0	8.7 ~ 9.0	8.8 ~ 9.2	8.8~9.2
Electrical conductivity at 25 °C in micro mhos/cm	< 0.5	< 0.5	< 0.4	< 0.3	< 0.2
Economizer inlet	< 0.01	< 0.01	< 0.005	< 0.005	< 0.005
Total iron (Fe ppm)	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01
Total copper (Cu ppm)	< 0.005	< 0.005	< 0.003	< 0.003	< 0.003
Total iron copper & nickel ppm	< 0.03	< 0.02	< 0.02	< 0.02	< 0.01
Total silica (SiO2 ppm)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01
Carbonic acid (CO2 ppm)	Nil	Nil	Nil	Nil	Nil
Organic matter mg KmnO4/Litre	Less than 0.1 ppm is considered tolerable				
Oil ppm	Nil	Nil	Nil	Nil	Nil
Hydrazine N_2H_4 ppm)	< 0.1	< 0.05	< 0.05	< 0.02 ~ 0.05	< 0.02

Boiler water :

General requirements : The sample collected through CBD line should flow continuously at a steady rate through a cooler. Temperature of the well condensed sample should not be more than 25 °C. There should be no appearance of red water when the flow is disturbed. Sample collection with partial choking of line can lead to misleading results. Lines may get choked with ferric and magnetic oxides. These oxides behave like weak ion exchange resins and render the sample's representation poor.

Boiler drum pressure kg/cm^2	60	80	100	120	130 & above
Electrical conductivity micro mhos/cm at 25 °C	< 300	< 200	< 100	< 50	< 50
Total solids (ppm)	< 125	< 75	< 50	< 20	< 15

pH at 25 °C	10.0 ~ 10.5	9.8 ~ 10.2	9.8 ~ 10.2	9.4 ~ 9.7	9.4 ~ 9.7
Total silica (SiO$_2$ ppm)	< 5	< 3	< 1.8	< 1.0	< 0.5

< 0.3 above 130Kg/Cm2

Phosphate (PO$_4$ ppm)	7.0 ~ 11.0	5.0 ~ 10.0	5.0 ~ 10.0	3.0 ~ 6.0	3.0 ~ 6.0
Chloride (NaCl ppm)	< 5.0	< 5.0	< 3.0	< 3.0	< 2.0

Free Hydroxide   To keep practically free
(NaOH ppm)

Phenolpthalene alkalinity (CaCO$_3$ ppm)	< 25	< 15	< 10	< 5	< 3

Conductivity:
Conductivity should be measured at 25 °C at continuously flowing local point.

pH :
It is necessary to maintain pH/PO$_4$ in accordance with coordinate control technique. Na to PO$_4$ ratio should be 3:1. For drum pressure rating of 130 Kg/Cm2 and above congruent control is preferable. Here Na to PO4 ratio is kept at 2.6:1. Ideal range is 2.6/2.8 to 1; a combination of trisodium

phosphates and disodium phosphates or sodium hexameta phosphate and sodium hydroxide is used to pH/PO$_4$ relation.

Chloride:

Presence of chloride is not desirable. Chloride ion impairs magnetite layer's growth and coherence. It retards healing mechanism. Even neutral or alkaline chloride may produce acid. It is desirable to shut the unit if chloride ingress is from cooling water leakage, D.M. plant leakage or from impure chemicals. In case of chloride contamination, adequate pH and b/d control becomes necessary till normalcy is restored.

Free Hydroxide:

Free hydroxide should be maintained as low as possible, made practically free by adopting coordinate/congruent technique. Na to PO$_4$ ratio at 2.8 to 1, under normal operating condition without any sulphate/chloride contamination, is ideal.

Saturated and Superheated Steam:

The objective is to obtain steam of very high purity, without any contamination from dissolved and entrained solids and acidic gasses, in order to prevent fouling of super heaters and turbine blades. Besides, the steam generated should be non corrosive to ferrous and copper alloys and conducive to the preservation of protective Fe/cu passive oxide layers.

Broad guide lines :

Solids ppm in steam	Turbine blade deposition	Super heater deposition
< 0.01	No	No
0.01 to 0.1	Possible	No
0.1 to 1.0	Yes	Possible
> 1.0	Yes	Yes

Steam sample should be collected through a well designed sampling device and cooler, so that the sample collected is well condensed to a temperature of 25 °C without suffering solid separation or concentration.

pH at 25 °C	8.9 to 9.2

The range is prescribed just to provide a safe guide line. It cannot be provided with certainty for want of reliable and established data. However, to a great extent, pH corresponding to a quantity of ammonia present in the steam, which when condensed shall not exceed an average value of 0.5 ppm in the return condensate and at any time a maximum value of 1.0 ppm can be relied upon. In the absence of carbon dioxide the recommendation made is reliable and workable.

Electrical conductivity	< 0.3 and < 0.2 is ideal

Micro mhos/cm at 25 °C	

Conductivity is measured at 25 °C at local continuous flow sampling point at the down stream of a strong cation exchanger. Sample at a constant flow rate is passed through a closed cell having no access to atmosphere. This in valid for CO_2 free sample only. If CO_2 is present, correction to the effect may give a value which may not be very reliable and accurate.

Sodium and potassium (ppm)   < 0.01 (less than 0.005 in case of austenitic parts.)
Total copper (Cu ppm)   < 0.003
Total iron (Fe ppm)   < 0.02
Total silica (SiO_2 ppm)   < 0.02 and < 0.01 ideal

Examples

Q.   What is the meaning of pH in water chemistry?

A.   It is a number between 0 and 14 indicating the degree of acidity or alkalinity. The pH scale resembles a thermometer scale, but the pH scale indicates intensity of acidity or alkalinity. The midpoint of the pH scale is 7, and a solution with this pH I neutral. Numbers below 7 denote acidity; those above, alkalinity. Since pH is a logarithmic function, solutions having a pH of 6.0, 5.0, or 4.0 are 10,100 or 1,000 times more acid than one with a pH of 7.0.

Q.   What is the reason for water hardness?

A.   Hardness of water is due to the presence of calcium and magnesium salts: bicarbonates, carbonates, chlorides, sulphates and nitrates. Presence of iron, aluminium and manganese salts also contributes to water hardness, but normally these are not present in appreciable quantities. Normal carbonates are also found, but only occasionally and in highly alkaline water. Nitrates are usually present in minor quantities while it has been found that sulphates on the average exceed chlorides.

Q.   What is carryover and how is it caused?

A.   Carryover is entrained moisture and associated solids passing from a boiler with the steam. These slugs of moisture cause erratic superheat and mechanical troubles with engines and turbines. Carryover also deposits solids in superheaters and on turbine blades. And it may even spoil materials in process. But the main causes of carryover are priming, foaming or both.

Q.   What is internal treatment?

A.   Treating water in the boiler while evaporation is taking place. The aim is to chemically adjust, or balance, the boiler water to prevent scale formation, corrosion, steam contamination, and embrittlement.

Q.   Explain priming of boiler water.

A.   Priming is the spouting or surging of water into the steam outlet. It is caused by too high a water level, uneven fire distribution, load swings, too high a steaming rate, or even faulty boiler design. Remedies range from redesigning the boiler or steam drum to installing steam purities, lowering the water level, improving firing distribution, or reducing the boiler load. Chemical antifoams also help.

Q. Do packaged boilers need high-quality feedwater?

A. Yes. These units don't require higher-quality feedwater than conventional boilers run at equivalent ratings, but clean boiler surfaces are more critical when operating at high evaporation rates. Scale builds up at a more rapid pace, and their smaller steam space promotes priming and foaming. Therefore, treatment must be carefully selected and controlled to produce high-quality feedwater. Don't compare packaged boilers with older steam generators run at much lower ratings. These older units sometimes do get with minimum attention to feedwater treatment.

Q. What is the basis of water softening by the precipitation method?

A. The scale forming cations Ca^{2+} and Mg^{2+} are precipitated from water by binding them with anions like CO_3^{2-} and OH^- to produce less soluble compounds, viz. $CaCO_3$, $MgCO_3$ and $Mg(OH)_2$ so the most of these harmful cations are eliminated from the system.

Q. Does hydrazine only eliminate dissolved oxygen when treated with boiler feedwater?

A. Apart from binding dissolved free oxygen in water, hydrazine also reduces oxides of iron and copper formed due to corrosion of metal.

$6Fe_2O_3 + N_2H_4 \rightarrow 4FeO_4 + N_2 + 2H_2O$
$2CuO + N_2H_4 \rightarrow 2Cu + N_2 + 2H_2O$
It also reduces ferric hydroxide to ferrous hydroxide.
$4Fe(OH)_3 + N_2H_4 \rightarrow 4Fe(OH)_2 + N_2 + 4H_2O$
and curbs the nitrite corrosion in high-pressure boiler units.

Q. Describe the zeolite softening processes for water treatment.

A. Ion-exchange resins are used at high temperatures for the hot-lime zeolite method. Effluent hardness is zero compared with 27 ppm excess soda ash is needed to produce this residual hardness. The resulting alkalinity is in the range of 45 to 50 ppm. Alkalinity from hot-lime-zeolite runs from 12 to 25 ppm. The residual hardness is removed by a hot zeolite. It is less costly from the chemical angle to remove this hardness with salt in a cation exchanger than with soda ash in the hot-process settling tank.

Examples for practice

Q.1 Write short notes on any one method of water treatment.

Q.2 State the difference between water softening and demineralising process. Which process is suitable for high pressure boilers and why?

Q.3 Write short notes on the following boiler problems, stating their reasons and remedial actions to be taken to prevent them
Foaming and Priming

Q.4 What is hard water? Describe any one method to remove permanent hardness?

Q.5 Why is it necessary to maintain the deaerated temperature equal to the saturation temperature of water corresponding to the pressure in the deaerator?

Q.6 What is the basis of chemical de-oxygenation of water?

Q.7 Differentiate between the followings.
Hardwater v/s Softwater

Q.8 Write SHORT NOTES
pH value and its importance in steam generation.

Q.9 What are usual impurities in the water for use in a boiler. Explain the terms temporary and permanent hardness of water and means adopted to remove them?

Q.10 Answer the following:
(i) What are the usual impurities in feed water?
(ii) What do you understand by the term 'pH' value?
(iii) What should be the range of this permissible pH value for feed water?

Q.11 Write short notes:
(a) Zeolite process of water softening (c) Priming and foaming (d) Internal treatment of boiler

Q.12 What is deaeration? State different types of deaeration processes. Explain with neat sketch thermal deaerator?

Q.13 State the difference between water softening and demineralising process. Which process is suitable for high pressure boilers and why?

Q.14 Boiler feed water treatment for HP boilers