WATER CONDITIONING

Chapter 3

pp. 19 -35

Why Water Conditioning

- ☐ Water conditioning and waste water purification is an essential function according to moral, legal, and environmental considerations.
- ☐ Industrial waste water presents a challenge that is considered a key operating expense.
- ☐ Some solutions: reuse of waste water, recovery of by-products to reduce cost of treatment, control of pollution.
- ☐ Water quality varies by location (also surface vs. ground water).

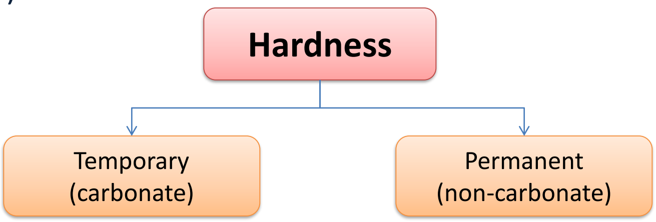
Hard Water

- ❑ ***Hard water*** is defined as that containing un-desirable amounts of dissolved salts of Ca and Mg, present as bicabronates, chlorides, sulfates, and nitrates.

- ❑ **Additional impurities in water**
  - Na salts, silica, alumina, iron, or manganese may present.
  - suspended insoluble matter (called ***Turbidity***)
  - Organic matter
  - Dissolved gases (CO_2, O_2, N_2, H_2S)

Types of Hardness

Hardness is expressed in terms of the dissolved Ca and Mg salts calculated as Ca carbonate equivalent (ppm, grain/gal, mg/L).



Hardness

Temporary (carbonate)

- caused by bicarbonates of Ca and Mg.
- greatly reduced by heating

Permanent (non-carbonate)

- caused by sulfates and chlorides of Ca and Mg
- reduced by chemicals

Terminology

- ❑ ***Total Dissolved Solids (TDS)***: unit ppm
  Range of TDS: few ppm – thousands ppm
- ❑ ***Unit of Hardness*** (measured as if all is due to Ca carbonate)
  - ppm
  - mg/L
  - grain /gal = 17.1 mg/L
- ❑ ***Turbidity***
  suspended insoluble matter in water
- ❑ ***Softening***
  processes which remove or reduce hardness of water
- ❑ ***Purification***
  Removal of organic matter and microorganisms from water.

Problems of Hard Water

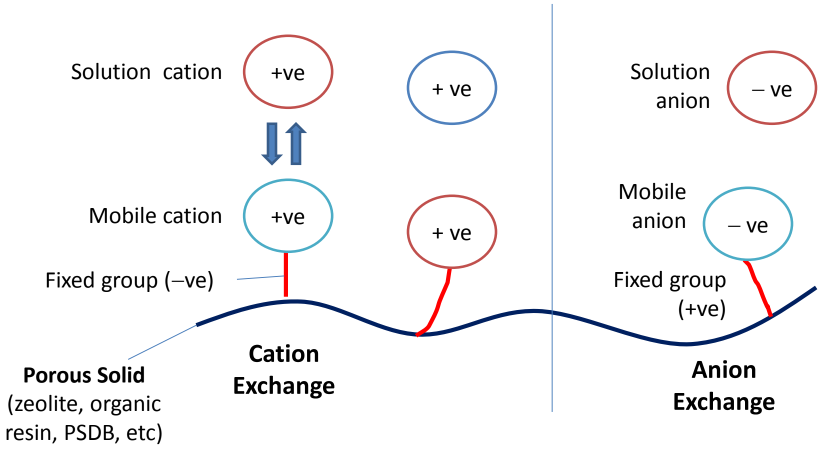
- ❑ Salts of Ca and Mg give insoluble precipitates with soap
- ❑ Ca sulfate, Ca carbonate, and Ca silicate form clogging scales with low thermal conductivity on boilers.
- ❑ Mg silicate and Ca carbonate may reduce heat transfer in process heat exchangers.
- ❑ **Treated waste water can be reused for:**
  - agriculture,
  - cooling and process water
  - Non-potable domestic applications.

Methods of Water Conditioning

1) Ion exchange
2) Lime-Soda process
3) Phosphate conditioning
4) Silica removal
5) De-aeration
6) Demineralization and desalting
7) Purification

(1) Ion Exchange

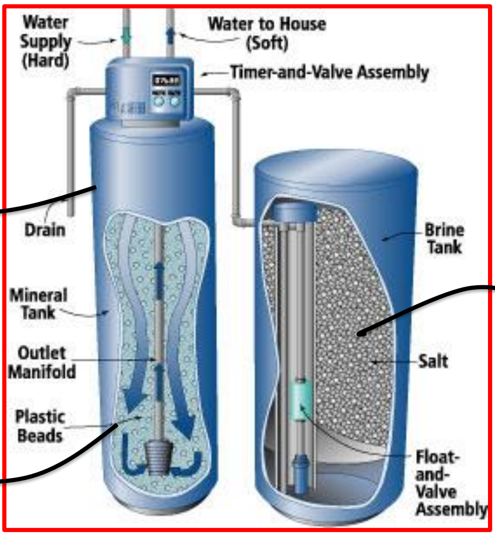
- **Ion exchange** is a chemical reaction in which a mobile hydrated ions are exchanged, equivalent for equivalent, for ions of like charge in the solution.



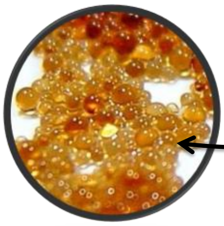
Ion Exchange

Water Softener

Commercial softener



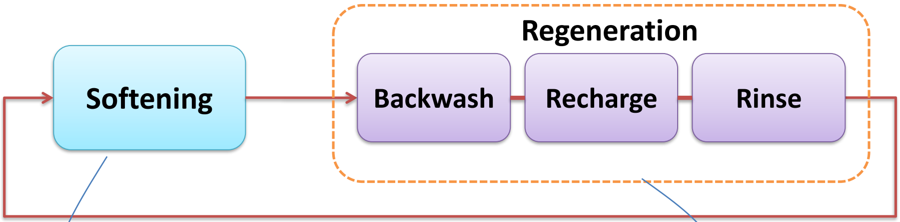
Ion exchange resin



Regeneration salt used to prepare brine solution

Ion Exchange

Water Softening Operation



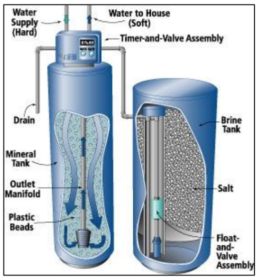
Softening

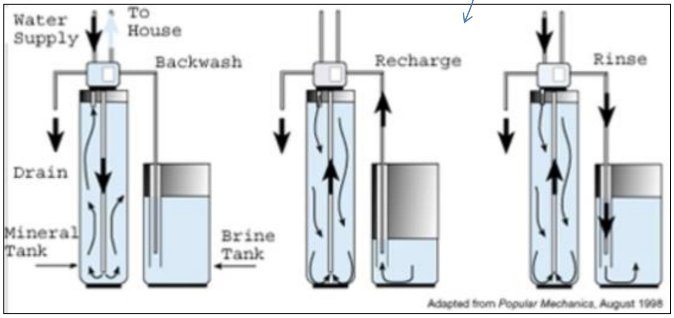
Regeneration

Backwash

Recharge

Rinse





Adapted from Popular Mechanics, August 1998

Na – Cation Exchange

(to remove Ca and Mg cations)

Softening: uses high capacity ion-exchange resins like Polystyrene

$$\left.\begin{matrix}Ca\\Mg\end{matrix}\right\}\left\{\begin{matrix}(HCO_3)_2\\SO_4\\Cl_2\end{matrix}\right. + 2NaR \rightarrow \left.\begin{matrix}Ca\\Mg\end{matrix}\right\}R_2 + Na_2\left\{\begin{matrix}(HCO_3)_2\\SO_4\\Cl_2\end{matrix}\right.$$

(soluble) **Hard water**	(insoluble) **Fresh resin**	(insoluble) **Used resin**	(soluble) **Soft water**

Regeneration: uses NaCl brine solution

$$\left.\begin{matrix}Ca\\Mg\end{matrix}\right\}R_2 + 2NaCl \rightarrow 2NaR + \left.\begin{matrix}Ca\\Mg\end{matrix}\right\}Cl_2$$

(insoluble) **Used resin**	(soluble) **Brine**	(insoluble) **Fresh resin**	(soluble) **waste**

H – Cation Exchange

(to remove ALL cations)

Reaction with bicarbonates

$$\left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}(HCO_3)_2 + 2HR \rightarrow \left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}R_2 + \underset{\text{water}}{2H_2O} + \underset{\text{Carbon dioxide}}{2CO_2}$$

(soluble)	(insoluble) **Fresh resin**	(insoluble) **Used resin**

Reaction with sulfate and chlorides

$$\left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}\left\{\begin{matrix}SO_4\\Cl_2\end{matrix}\right. + 2HR \rightarrow \left.\begin{matrix}Ca\\Mg\\Na_2\end{matrix}\right\}R_2 + H_2\left\{\begin{matrix}SO_4\\Cl_2\end{matrix}\right.$$

to be neutralized

(soluble)	(insoluble) **Resin**	(insoluble) **Used resin**	(soluble) **Acidic water**

H – Cation Exchange cont'd

(to remove ALL cations)

Regeneration: using sulfuric acid (H_2SO_4)

$$\left.\begin{matrix} Ca \\ Mg \\ Na_2 \end{matrix}\right\} R_2 \quad + \quad H_2SO_4 \quad \rightarrow 2HR \quad + \quad \left.\begin{matrix} Ca \\ Mg \\ Na_2 \end{matrix}\right\} SO_4$$

(insoluble)	(soluble)	(insoluble)	(soluble)
Used resin		**fresh resin**	**waste**

(2) Lime-Soda Process

- **Lime-Soda process:** is a chemical reaction used to reduce hardness from water.
- **Lime** = $Ca(OH)_2$ **Soda ash**= Na_2CO_3
- This process is now obsolete but was very useful for the treatment of large volumes of hard water.
- Addition of lime ($Ca(OH)_2$) and soda (Na_2CO_3) to the hard water precipitates calcium as the carbonate ($CaCO_3$), and magnesium as hydroxide ($Mg(OH)_2$).

Types of Lime-Soda Process

Cold lime process

- Partial softening → uses cheap lime.
- For conditioning cooling water that contains Ca bicarbonate (scale former), and paper mill water.
- Needs addition of coagulants
- Disadvantages: produces bulk amounts of sludge; disposal is expensive and troublesome.

Hot lime process

- For conditioning boiler feed water.
- Operates at a higher temperature so reactions, coagulation and precipitation are faster, and gases are driven out.

Lime Process Reactions

- As lime is added to a water, it will react with any carbon dioxide present as follows:
  $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$ ....(1)
- The lime will react with carbonate hardness as follows:
  $Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$ .....(2)
  $Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow \underline{MgCO_3} + CaCO_3 \downarrow + 2H_2O$ .....(3)
- The <u>MgCO3</u> in eq (3) is soluble, so more lime is added to remove it:
  $Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3 \downarrow + Mg(OH)_2 \downarrow$ .....(4)
- Also, magnesium non-carbonate hardness, such as magnesium sulfate, is removed:
  $Ca(OH)_2 + MgSO_4 \rightarrow \underline{CaSO_4} + Mg(OH)_2 \downarrow$ .....(5)

Soda Process Reactions

- Lime addition removes only magnesium hardness and calcium carbonate hardness.
- In equation 5 magnesium is removed ($MgSO_4$), however, an equivalent amount of calcium is added as $CaSO_4$.
- The water now contains the original calcium non-carbonate hardness and the calcium non-carbonate hardness produced in equation 5. Soda ash is added to remove calcium non-carbonate hardness:

$$Na_2CO_3 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3 \downarrow \quad ....(6)$$

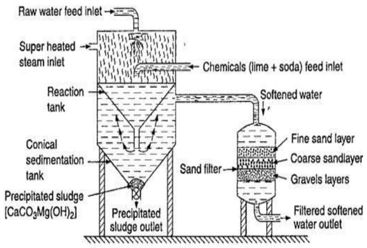
Hot Lime Soda Process

- The water to be purified is treated with chemicals at a temperature of 95-100°C. Softeners used may be intermittent or continuous type.

(a) Intermittent type (Batch process)

- Similar to the cold lime soda process except that heating coils are present for heating the water.

(b) Continuous type

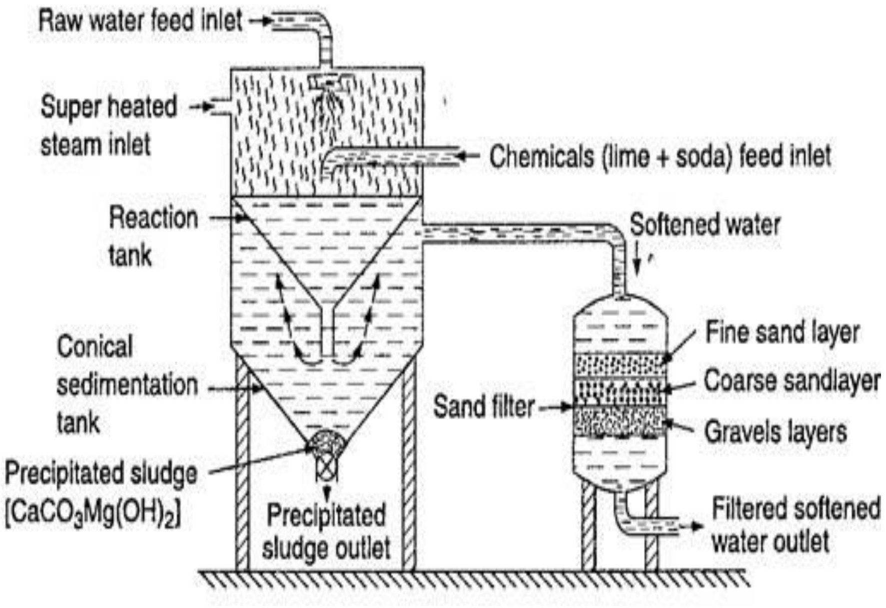


Hot Lime Soda Process
(b) Continuous type

It has the following parts:

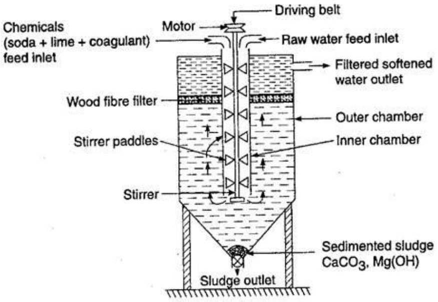
i. Reactiom tank: The central reaction tank has three separate inlets through which raw water, chemicals and superheated steam is passed and then mixed together in the reaction tank.
ii. Conical sedimentation tank: In this tank the mixed water enters and the sludge settles down.
iii. Sand filter: Layers of coarse and fine sand act as filter which ensures complete removal of sludge. A soft water with 15-30 ppm of residual hardness is obtained.

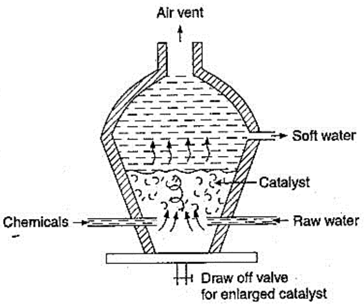
Reference:
http://www.google.jo/imgres?um=1&hl=ar&sa=N&tbm=isch&tbnid=CatIAnEGXd9scM:&imgrefurl=http://www.transtutors.com/homework-help/engineering-chemistry/softening-of-water/hot-lime-soda.aspx&docid=3Z9b78e9aosqRM&imgurl=http://www.transtutors.com/Uploadfile/CMS_Images/15735_image007.jpg&w=514&h=264&ei=moFsUJHDDY23hAfxjICABw&zoom=1&iact=hc&vpx=266&vpy=167&dur=4259&hovh=161&hovw=313&tx=173&ty=98&sig=106643344963619828316&page=1&tbnh=136&tbnw=262&start=0&ndsp=16&ved=1t:429,r:3,s:0,i:75&biw=1241&bih=615



Continuous Cold Lime Soda Softeners

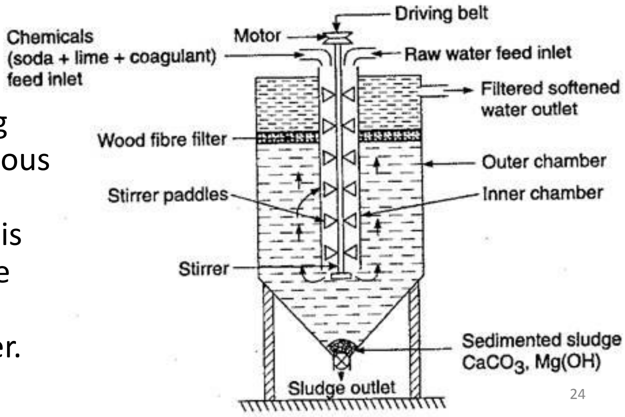
i. Conventional type
ii. The sludge blanket type
iii. Catalyst or Separator type





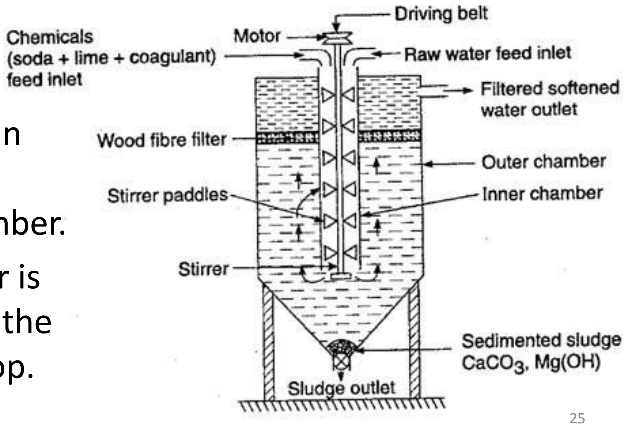
Continuous Cold Lime Soda Softeners
(i) Conventional type

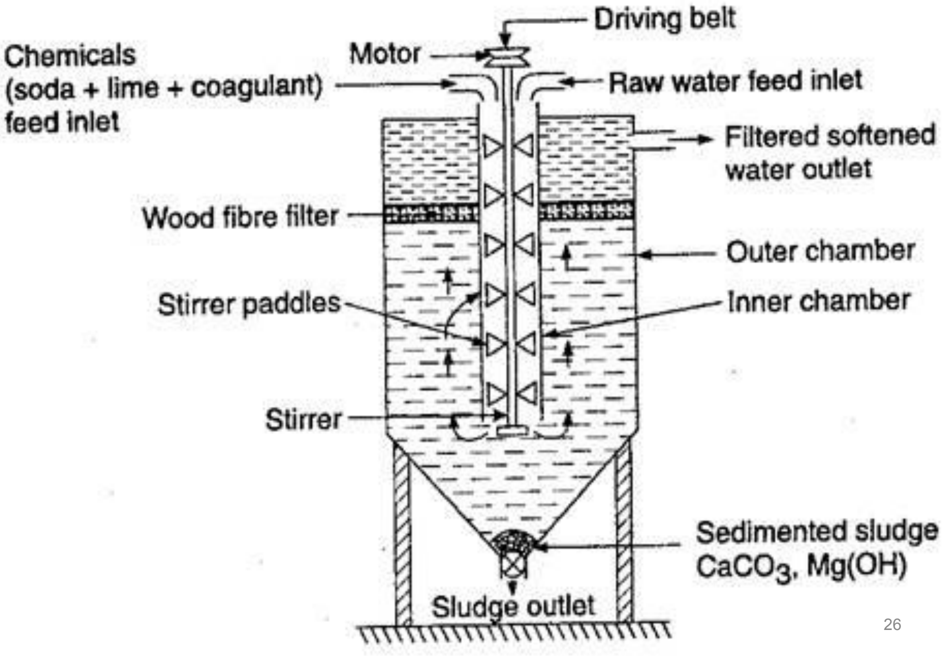
- Raw water and the required amount of lime, soda and coagulants are fed at room temperature from the top into the inner vertical circular chamber fitted with a paddle stirrer.
- Vigorous stirring ensures continuous mixing;
- Softened water is allowed to come into the outer co-axial chamber.



Continuous Cold Lime Soda Softeners
(i) Conventional type

- Rising up the water passes through a wood fiber filter where traces of sludge are removed.
- Sludge settles in the bottom of the outer chamber.
- Softened water is removed from the outlet at the top.





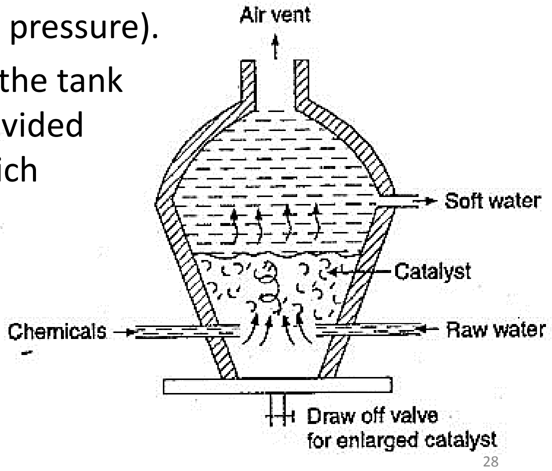
Continuous Cold Lime Soda Softeners
(ii) Sludge Blanket type

- It is similar to the conventional type but the treated water is filtered upwardly through a suspended sludge blanket composed of-previously formed precipitates.
- Some lime is wasted in the conventional type as is carried down with the sludge before it has time for dissolution and reaction.
- Silica is better removed in sludge blanket type.
- Retention time required is one hour as compared to four hours for the conventional.

Reference:
http://www.transtutors.com/homework-help/engineering-chemistry/softening-of-water/continuous-softeners.aspx

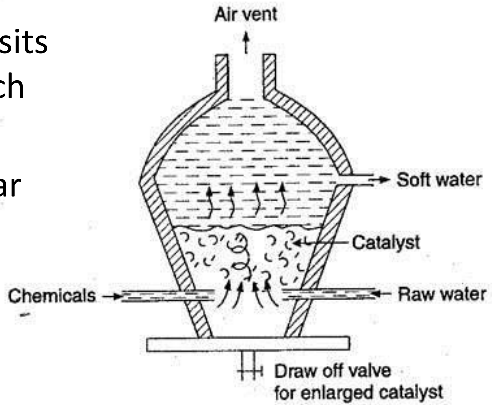
Continuous Cold Lime Soda Softeners
(iii) Catalyst or Separator type

- A conical tank is used which may be open (for gravity operation) or closed (for operation under pressure).
- About two-thirds of the tank is filled with finely divided granular catalyst which may be green sand or sand or graded calcite.



Continuous Cold Lime Soda Softeners (iii) Catalyst or Separator type

- Raw water and chemicals enter tangentially near bottom and spiral upwards through suspended catalyst bed.
- The sludge formed deposits on granular catalyst which grows in size.
- Sludge formed in granular shape can be drained and dried rapidly, which also makes it easy to handle.



Soda Process Reactions

- Precipitation of $CaCO_3$ requires a pH of about 9.5; while $Mg(OH)_2$ requires a 10.8 pH, therefore, an excess lime of about 1.25 meq/l is required to raise the pH.
- The amount of lime required: lime (meq/l) = carbon dioxide (meq/l) + carbonate hardness (meq/l) + magnesium ion (meq/l) + 1.25 (meq/l)
- The amount of soda ash required: soda ash (meq/l) = non-carbonate hardness (meq/l).
- After softening, the water will have high pH and contain the excess lime and the magnesium hydroxide and the calcium carbonate that did not precipitate

Recarbonation

- Recarbonation (adding carbon dioxide) is used to stabilize the water. The excess lime and magnesium hydroxide are stabilized by adding carbon dioxide, which also reduces pH from 10.8 to 9.5 as the following:

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

$$\mathbf{CO_2 + Mg(OH)_2 \rightarrow \underline{MgCO_3} + H_2O}$$

- Further recarbonation, will bring the pH to about 8.5 and stabilize the calcium carbonate as the following:

$$\mathbf{CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2}$$

- It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

Chemical handling and sludge handling are critical issues in Lime Soda Softening.

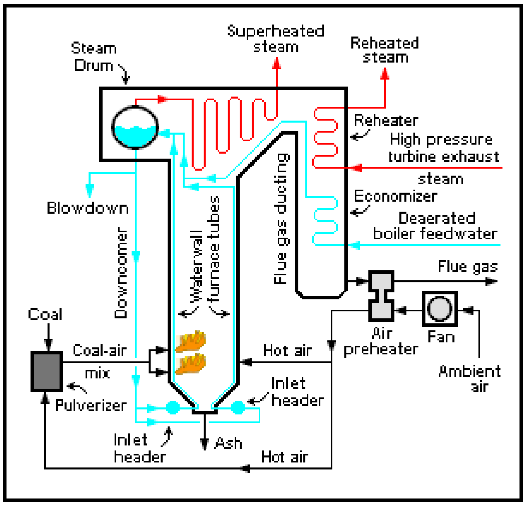
Water Softening Unit

References:

http://textilelearner.blogspot.com/2012/06/lime-soda-water-softening-process.html#ixzz27b9iadUH
http://textilelearner.blogspot.com/2012/06/lime-soda-water-softening-process.html

(3) Phosphate Conditioning

Purpose :
To ***internally*** remove Ca and Mg as sludge from boiler water in high pressure boilers for steam generation plants.



http://en.wikipedia.org/wiki/File:Steam_Generator.png

Why Ca^{+2} & Mg^{+2} should be removed?

1. They precipitates as scales, e.g., $CaSO_4$, $CaCO_3$, SiO_2 and $Mg(OH)_2$ fused together.
2. Scales retards in heat transfer processes
3. Also overheating causes failure of metals.

Boiler scale on water side

http://www.lenntech.ae/applications/process/boiler/scaling.htm

Phosphate Conditioning

How to prevent scales?

1. By adding soluble phosphate to boiling water (10-60) ppm; depends on the operating conditions. This forms a sludge that can be removed subsequently by a blow down operation.
2. Blow down: To control the concentration of one or more natural components of boiler water (it removes solids in concentrated solutions).

Phosphate Conditioning

How to prevent scales ?

- The amount of reserve phosphate required in boiler water depends upon the calcium content of the feed water, boiler pressure and the type of boilers involved, blow down procedure, and the chemical feeding method employed.
- Maximum and minimum phosphate control limits are normally 10-60 ppm. Loss of the reserve of the phosphate must almost inevitably result in deposition of calcium scale. Therefore, you should never hesitate to increase the feed of phosphate whenever boiler water phosphate concentrations run near or below the specified minimum.

Phosphate Conditioning

Types of Phosphates Used

Different sodium phosphates are used:

- Orthophosphates, such as trisodium phosphate
- Complex phosphates, such as sodium hexametaphosphate

Sodium phosphates are widely used to:

1. Inhibit $CaCO_3$ precipitation in heated water.
2. Minimize corrosion and pickup of iron by water in:
    a. Circulating cooling water
    b. Plant water distribution system
    c. Municipal systems

Phosphate Conditioning

Types of Phosphates Used

Different *orthophosphates* are used depending on pH of the boiler water:

1. Sodium dihydrogen phosphate (acidic) NaH_2PO_4

$$3CaCO_3 + 2NaH_2PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + Na_2CO_3 + 2H_2O + 2CO_2$$

2. Disodium hydrogen phosphate (weakly acidic) Na_2HPO_4

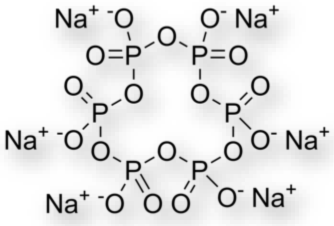
3. Trisodium hydrogen phosphate (alkaline) Na_3PO_4.

$$3CaSO_4 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 3Na_2SO_4$$

$$3Mg(OH)_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2\downarrow + 3Na_2SO_4$$

www.expertsmind.com; Chemistry of engineers book-page 92

Sodium Hexametaphosphate $(NaPO_3)_6$



- a commonly used source of orthophosphate anion used to precipitate calcium in low pressure boilers.
- With dispersants the calcium phosphate becomes a fluidized sludge capable of being blown down and out of the boiler before the calcium can form a deposit.

(4) Silica Removal

- Silica is *not* removed by H-cation or Na-cation exchange.
- Silica is *partially* removed in lime-soda process.
- It can form a *tenacious scale*.
- It can be removed by:
  - the use of dolomitic lime $CaMg(CO_3)_2$ or activated magnesia in the softener, which lowers silica concentration, then blowdown is applied.
  - Demineralization, which produces water with only traces of silica.

(5) Deaeration

- Necessary to condition water properly for industrial boiler use.
- Dissolved oxygen hastens corrosion.

- Iron water corrosion accelerated by oxygen under alkaline or neutral conditions:

$Fe \rightarrow Fe^{2+} + 2e$ (anodic half reaction)

$O_2 + 2H_2O + 4e \rightarrow 4OH^-$ (cathode half reaction)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$ (overall reaction)

Deaeration

How to Stop the Corrosion?

- By removal of dissolved oxygen.
- By electrode polarization.
- By organic inhibitors.
- By protective salts: chromates, silicates, phosphates, alkalies
  - They act as anodic inhibitor by forming a film over the anodic side, and thus interrupt the electrochemical sequence.

Deaeration

How to Remove Dissolved Oxygen?

- By spraying or cascading the water over a series of trays contained in pressurized vessel, with steam rising upward.
  - **In closed deaerating heaters (105 °C):**
    dissolved O_2 content will be lowered to below 10^{-2} ppm.

- Complete deoxygenation can be achieved by using **oxygen scavengers**:

Sodium sulfite: $O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$

Hydrazine hydrate: $O_2 + N_2H_4 \cdot H_2O \rightarrow 3H_2O + N_2$

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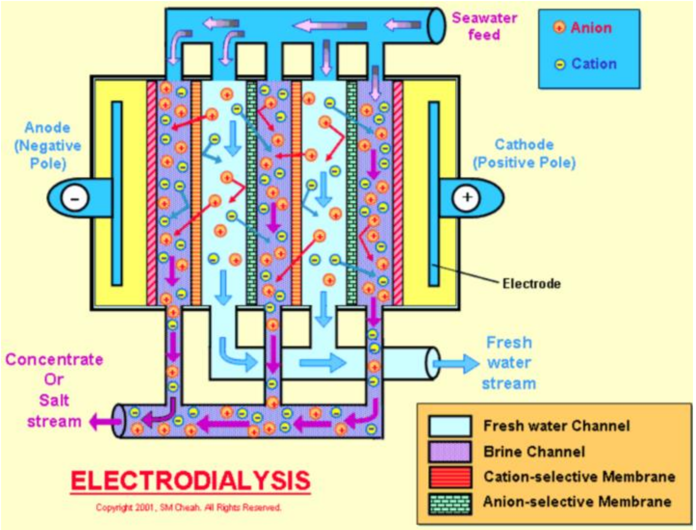
(6) Demineralization & Desalting

- Read the related section in Shereve’s textbook and answer the following questions:
  - What is the difference between partial and complete desalting processes?
  - Write down 6 different methods used for desalting.
  - Define the performance ratio.
  - The book states that the largest desalination plant in the world is being built near Yuma, Ariz, and is designed for a capacity of 360,000 m^3/day. What and where is the largest desalination plant in the world nowadays? What is its capacity. Write a one page (~300 words) summary about that desalination plant.

Demineralization & Desalting

Electrodialysis (ED)



Reference: http://www.separationprocesses.com/Membrane/MT_ChpED-1.htm

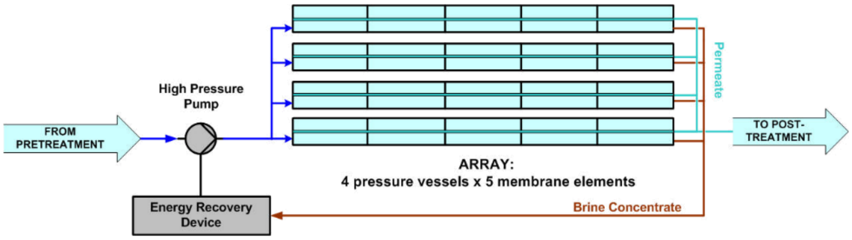
Demineralization & Desalting

Reverse Osmosis (RO)

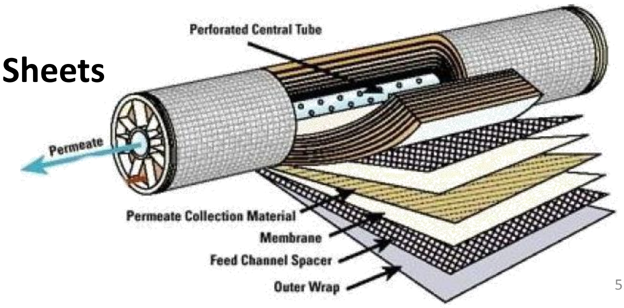
- Utilizes the application of pressure above the osmotic pressure to force pure water through a semipermeable membrane from the concentrated brine solution.
- **Two types of membranes:**
  - Bundles of very fine capillaries
  - Spiral-wound sheets
- **Membranes material:**
  - Cellulose acetate → for brackish water
  - Polyamides → for seawater

Demineralization & Desalting

Reverse Osmosis (RO)



Spiral Wound Sheets



(7) Purification

- Usually necessary to produce potable and safe water
- Coagulation and filtration through sand or hard coal + oxidation by aeration → sufficient to remove organic matter (and some microorganisms)
- Further chlorine treatment might be needed

Study Figure 3.5 and make sure that you know what every and each unit is used for!