Function of lime $Ca(OH)_2$

(i) Removal of Temporary Calcium hardness & Mg hardness

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

(Soluble) PPT (Insoluble)

$$2 \times \left\{ Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca(HCO_3)_2 \right.$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow \underset{\text{ppt}}{CaCO_3} + H_2O$$

reacts 2 times

(ii) Removal of Permanent hardness

$$MgCl_2 + \underbrace{Ca(OH)_2}_{(Soda)} \rightarrow Mg(OH)_2 + CaCl_2$$

$$MgSO_4 + \underbrace{Ca(OH)_2}_{(Soda)} \rightarrow Mg(OH)_2 + CaSO_4$$

$$\cancel{CaSO_4} + \underbrace{Ca(OH)_2} \rightarrow CaSO_4 + Ca(OH)_2$$ | Same product

Lime will not remove permanent hardness

~~what is the~~ function of Soda (Na_2CO_3)

$$Na_2CO_3 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3$$ | Removes the ~~P~~ Permanent hardness

Thus: Lime: Temp. Ca hardness
(will remove): Temp Mg "
+ Parmant Mg "

Soda → Parmant Ca hardness
+ Permanant Mg hardness

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + \underline{CaCl_2}$$

if | CO_2 gas, acid, other salts ($FeSO_4$, $Al_2(SO_4)_3$

Lime-soda will remove

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

$Ca(OH)_2 + H_2S \rightarrow CaS + H_2O$

Acid

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$

(Permanent hardness)

$\downarrow$ $\boxed{\text{requires Soda}}$

$Na_2CO_3 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3$

Coagulant (e.g. $NaAlO_2$)

($CaCO_3$, $Mg(OH)_2$) ppts & collect together & make large particle

$\downarrow$

& settles down.

Cold Lime Soda Process	Hot Lime Soda Process
1. It is done at room temp (25-30°C)	1. It is done at elevated temp (94-100°C)
2. It is a slow process.	2. It is a rapid process
3. The use of coagulants is must	3. Coagulants not needed
4. Filtration is not easy	4. Filtration is easy (As viscosity of water becomes low at elevated temp)
5. Softened water has residual hardness around 60 ppm	5. Softened water has residual hardness of 15-30 ppm
6. Dissolved gases are not removed	6. Dissolved gases such as CO_2 are removed to some extent
7. Low softening capacity	7. High softening capacity

Calculations of Lime-Soda Requirements

Exp : Calculate the amount of ~~time~~ lime required for softening of 5000 liters of hard water containing 72 ppm of $MgSO_4$.

→ Given hard ~~water~~ water contains $MgSO_4$, so for its softening we require both lime & soda, according to the equation

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaSO_4 \quad \text{—(i)}$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4 \quad \text{—(ii)}$$

As asked only for lime amount, so eq (i) is imp.

Required of lime for 1 mole of $MgSO_4$ = 1 mole of $Ca(OH)_2$

or ⟶ 120 gm of $MgSO_4$ = 74 gm $Ca(OH)_2$

⟶ 72 ppm of $MgSO_4$ = $\frac{74}{120} \times 72$ ppm (mg/L) —(iii)

hence, for softening of 1L of water, lime required is = $\frac{74 \times 72}{120}$ mg

Thus for softening of 5000 L, lime required is

$$\frac{74 \times 72}{120} \times 5000 = 222000 \text{ mg} = 222 \text{ gm}$$

Lime requirement for softening (in mg/L)

$$= \frac{74}{100}\left[\begin{matrix} Ca(HCO_3)_2 \\ \text{or} \\ \text{Temporary } Ca^{2+} \end{matrix}\right] + \left[\begin{matrix} 2\,Mg(HCO_3)_2 \\ \text{or} \\ 2 \times \text{Temp } Mg^{2+} \end{matrix}\right] +$$

$$\text{Perm.}\left\{\left(\begin{matrix} Mg^{2+} \\ \text{or} \\ MgCl_2 / MgSO_4 \end{matrix}\right) + \left(\begin{matrix} Fe^{2+} \text{ or } FeSO_4 \\ \text{or} \\ FeSO_4 \cdot 7H_2O \end{matrix}\right) + \left(\begin{matrix} Al^{3+} \\ \text{or} \\ Al_2(SO_4)_3 \end{matrix}\right)\right\}$$

$$+ CO_2 + \left[\begin{matrix} H^+ / HCl \\ \text{or} \\ H_2SO_4 \end{matrix}\right] + \left[\begin{matrix} HCO_3^- \\ \text{or} \\ NaHCO_3 \end{matrix}\right] - NaAlO_2 \Big]$$

All in terms of $CaCO_3$ equivalents

Soda requirements for softening (in mg/L)

$$= \frac{106}{100}\left[\text{perm.}\begin{pmatrix} Ca^{2+} \text{ or } CaCl_2 \\ \text{or} \\ CaSO_4 \end{pmatrix} + \begin{pmatrix} Mg^{2+} \text{ or } MgCl_2 \\ \text{or} \\ MgSO_4 \end{pmatrix} + \left(Al^{3+} / Al_2(SO_4)_3\right) + \begin{bmatrix} Fe^{2+} \\ \text{or} \\ FeSO_4 \end{bmatrix} + \begin{pmatrix} H^{+} \\ \text{or} \\ HCl/H_2SO_4 \end{pmatrix} - \begin{bmatrix} HCO_3^{-} \\ \text{or} \\ NaHCO_3 \end{bmatrix}\right]$$

All in terms of $CaCO_3$ equivalent

Calculate the amount of lime required for softening 50,000 L of hard water containing $Mg(HCO_3)_2$ = 144 ppm, $Ca(HCO_3)_2$ = 25 ppm, $MgCl_2$ = 95 ppm, $CaCl_2$ = 111 ppm, Fe_2O_3 = 25 ppm, Na_2SO_4 = 15 ppm

Suppose, L stands for Lime $Ca(OH)_2$
S stands for soda Na_2CO_3

Constituent	Reactions	~~[illegible]~~	Neq
$Mg(HCO_3)_2$	$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$		2L
$Ca(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$		L
$MgCl_2$	$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2$		L
$CaCl_2$	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$		S

Fe_2O_3, Na_2SO_4 does not causes hardening so they donot need L or S

Thus, Lime requirement = $\frac{74}{100}$ [2 × $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ +

+ $MgCl_2$ in terms of $CaCO_3$ equivalent] × vol of water

Step I Conversion into $CaCO_3$ equivalent

	Amount	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$	144 ppm	100/146	$144 \times \frac{100}{146}$ = 98.6
$Ca(HCO_3)_2$	25 ppm	100/162	25 × 100/162 = 15.4 ppm
$MgCl_2$	95 ppm	100/95	95 × 100/95 = 100 ppm

Step II Lime requirement = $\frac{74}{100}$ [2 × 98.6 + 15.4 + 100] mg/L × 5000

= 115620 mg = 11.56 kg

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ADVANTAGES OF LIME-SODA PROCESS:

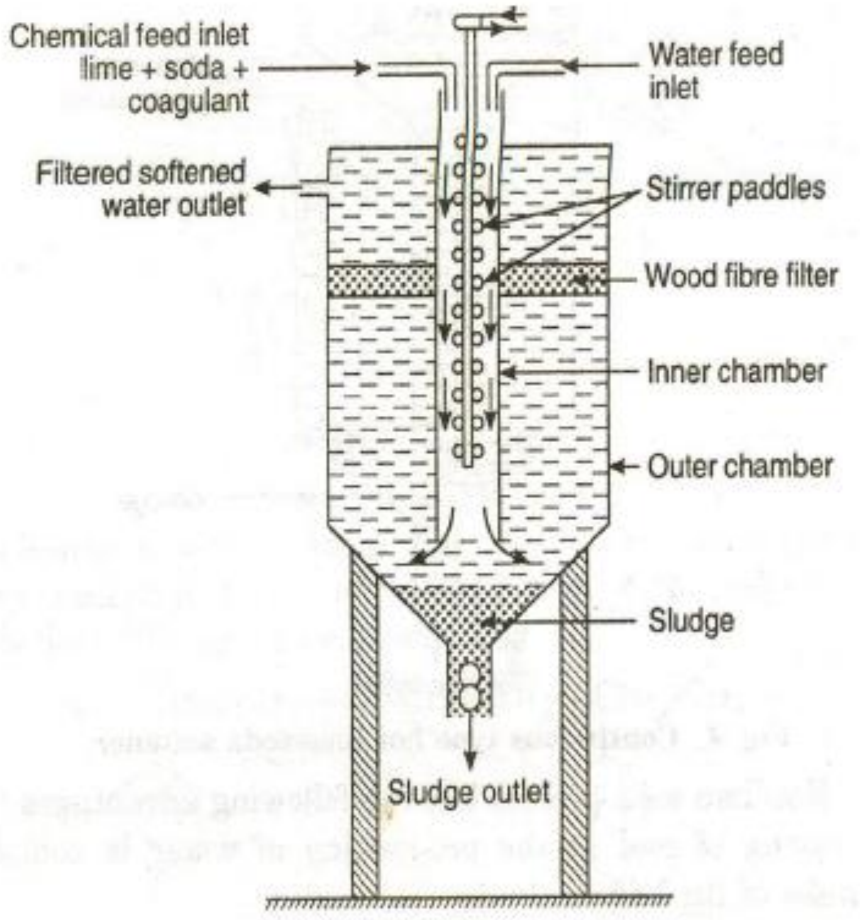
1. It is very economical
2. If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.
3. The process increases the pH value of the treated-water; thereby corrosion of the distribution pipes is reduced.
4. Besides the removal of harness, the quantity of minerals in the water is reduced.
5. To certain extent, iron and manganese are also removed from the water.
6. Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced.

DIS-ADVANTAGES OF LIME-SODA PROCESS:

1. For efficient and economical softening, careful operation and skilled supervision is required.
2. Disposal of large amounts of sludge or insoluble precipitates poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city.
3. This can remove hardness only up to 15 ppm, which is not good for boilers.

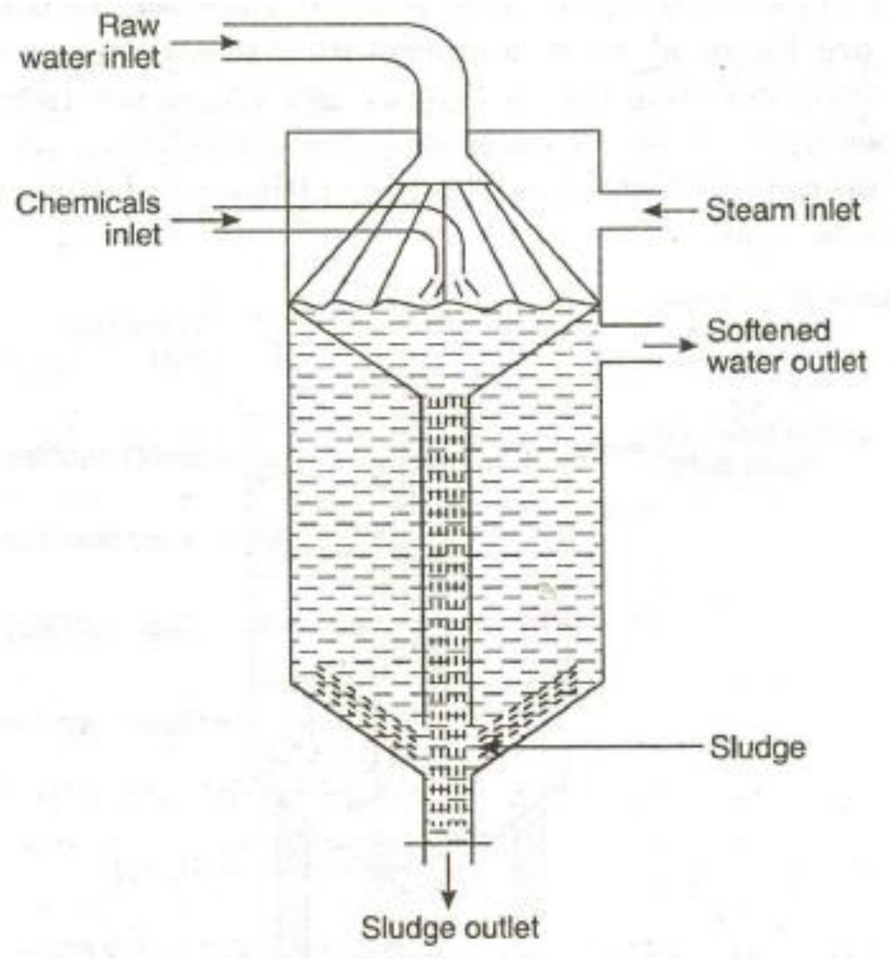
Cold Lime-soda process

- Calculated amount of lime/soda mixed with water at RT.
- Addition of coagulants to increase the size of precipitate.



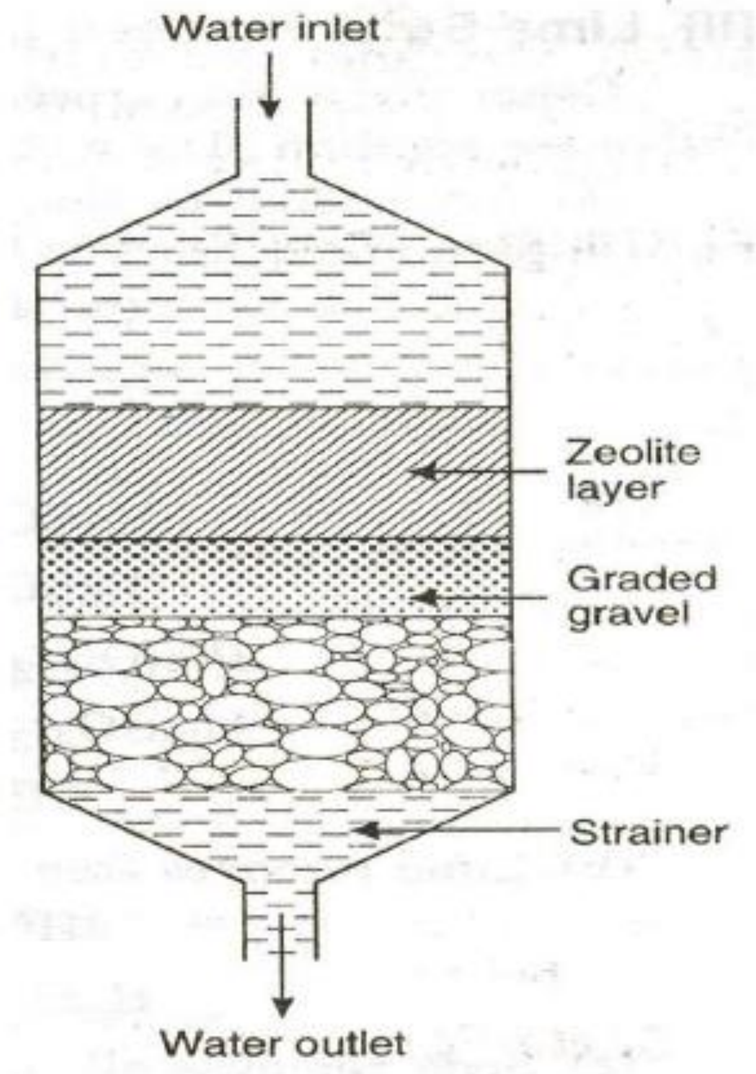
Hot L-S Process

- Reaction at 80-150˚C.
- Saving of coal.
- Required time is reduced.
- Requirement of chemicals is reduced.
- No coagulant is required.



2. Zeolite Process

- **Zeolite:** Sodium aluminium orthosilicate ($Na_2O.Al_2O_3.xSiO_2.yH_2O$) where, x = 2-10; y = 2-6.
- Natural or synthetic.
- Exchange their Na^+ ions by Ca^{+2} or Mg^{+2} ions in hard water.



Chemistry involved

$$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$$

$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$

$$CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$$

$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

$$MgCl_2 + Na_2Ze \longrightarrow \underset{\text{(Exhausted zeolite)}}{MgZe} + 2NaCl$$

Reusage of exhausted zeolite:

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \longrightarrow MgCl_2 + Na_2Ze$$

Q. The hardness of 10,000 Lit of a sample of water was removed by passing it through zeolite ~~softner~~. Softener. The zeolite softener then required 200 Lit of NaCl solution containing 150 mg / Lit of NaCl for regeneration. Find the hardness of water sample.

Sol: NaCl contained in 200 L of NaCl solution

$= \cancel{150\ gm/L} = 150\ gm/L \times 200\ L$

$= 30{,}000$ gm of NaCl

$= 30{,}000 \times \frac{50}{58.5} = 25{,}641$ gm equivalent of $CaCO_3$

10,000 Lit of water $= 25{,}641$ gm eq. of $CaCO_3$

1 L of water $= \frac{2.5641 \times 10^7}{10{,}000}$ mg/L of $CaCO_3$ eq

$\boxed{\text{Hence, hardness of water} = 2564\ ppm}$

Q. An exhausted zeolite softener was regenerated by passing 150 Lit of NaCl solution, having a strength of 150 gr/L of NaCl. Find the total vol. of water that can be softend by this zeolite softener, if the hardness of water is 500 ppm

Sol. 150 L of NaCl contains = $150 \times (150\ g/L)$ of NaCl

$= 22,500$ gm of NaCl

$= 22,500 \times \left(\frac{100}{117}\right)$ $CaCO_3$ eq

$= 1.932 \times 10^4$ gm $CaCO_3$ eq

$= 1.932 \times 10^7$ mg $CaCO_3$ eq

Let V Lit of 500 ppm (or 500 gm/L) water contains hardness

$= 1.932 \times 10^7$ mg $CaCO_3$ eq.

Number of litres of hard water, $V = \frac{1.932 \times 10^7}{500}$

$= \underline{\underline{38640\ L}}$

Q. A sample of water was analyzed & found to contain temporary magnesium hardness 25 mg / Lit. & permanent magnesium chloride hardness 15 mg / Lit. & permanent calcium sulfate hardness 20 mg / Lit, SiO_2 = 300 mg / lit. Calculate the lime & soda requirement for softening 30,000 Lit of hard water.

Solution Lime requirement

$$= \frac{74}{100}\left[2 \times \text{temp } Mg + MgCl_2 \text{ as } CaCO_3 \text{ eq}\right] \times \text{vol of water}$$

$$= \frac{74}{100}\left[2 \times 25 \times \frac{100}{24} + 15 \times \frac{100}{95}\right] mg/L \times 30,000 L \times \frac{1 gm}{10^3 mg}$$

$$= 4975.53 g$$

Soda requirement

$$= \frac{106}{100}\left[MgCl_2 + CaSO_4 \text{ as } CaCO_3 \text{ eq}\right] \times \text{vol of water}$$

$$= \frac{106}{100}\left[15 \times \frac{100}{95} + 20 \times \frac{100}{136}\right] mg/L \times 30,000 \times \frac{1 gm}{10^3 mg}$$

$$= 969.75 \text{ gm}$$

3. Calgon Process

- Calgon: Sodium hexametaphosfate [$Na_2P_6O_{18}$]

$$\underset{\text{Calgon}}{Na_2[Na_4(PO_3)_6]} \longrightarrow 2Na^+ + \underset{\text{Loose sludge}}{[Na_4P_6O_{18}]^{2-}}$$

$$[Na_4P_6O_{18}]^{2-} + 2CaCO_3 \longrightarrow \underset{\substack{\text{Soluble}\\ \text{complex ion}}}{[Ca_2P_6O_{18}]^{2-}} + 2Na_2CO_3$$

Lime-requirement for softening (in mg/L)

$$= \frac{74}{100}\left[\left(\begin{array}{c} Ca(HCO_3)_2 \\ \text{or} \\ \text{Temp. } Ca^{2+} \end{array}\right) + \left(\begin{array}{c} 2Mg(HCO_3)_2 \\ \text{or} \\ 2 \times \text{Temp. } Mg^{2+} \end{array}\right)\right.$$

$$+ \text{Perm.}\left\{\left(\begin{array}{c} Mg^{2+} \\ \text{or} \\ MgCl_2 \text{ or } MgSO_4 \end{array}\right) + \left(\begin{array}{c} Fe^{2+} \text{ or } FeSO_4 \\ \text{or} \\ FeSO_4 \cdot 7H_2O \end{array}\right) + \left(\begin{array}{c} Al^{3+} \\ \text{or} \\ Al_2(SO_4)_3 \end{array}\right)\right\}$$

$$\left. + CO_2 + \left(\begin{array}{c} H^+ \text{ or } HCl \\ \text{or} \\ H_2SO_4 \end{array}\right) + \left(\begin{array}{c} HCO_3^- \\ \text{or} \\ NaHCO_3 \end{array}\right) - NaAlO_2\right]$$ all in terms of $CaCO_3$ equivalents

and Soda requirement for softening (in mg/L)

$$= \frac{106}{100}\left[\text{perm.}\left(\begin{array}{c} Ca^{2+} \text{ or } CaCl_2 \\ \text{or} \\ CaSO_4 \end{array}\right) + \left(\begin{array}{c} Mg^{2+} \text{ or } MgCl_2 \\ \text{or} \\ MgSO_4 \end{array}\right)\right.$$

$$\left. + (Al^{3+} \text{ or } Al_2(SO_4)_3 + \left(\begin{array}{c} Fe^{2+} \\ \text{or} \\ FeSO_4 \end{array}\right) + \left(\begin{array}{c} H^+ \\ \text{or} \\ HCl \text{ or } H_2SO_4 \end{array}\right) - \left(\begin{array}{c} HCO_3^- \\ \text{or} \\ \text{or } NaHCO_3 \end{array}\right)\right]$$

all in terms of $CaCO_3$ equivalents.