## EN8491

## WATER SUPLLY ENGINEERING

## WATER SOFTENING LIME SODA PROCESS

## HARDNESS

- Hardness is defined as sum of divalent metallic cations existing in water such as;
- $\mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}, \mathrm{Fe}^{2+}, \mathrm{Mn}^{2+}$
- Practically most hardness is due to $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$ ions (the predominant minerals in natural waters)
- Total Hardness $=\mathrm{Ca}^{2+}$ hardness $+\mathrm{Mg}^{2+}$ hardness
- where the concentration of each ion is in consistent units such as $\mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO3}$, or meq/L.


## HARD WATER CLASSIFICATION

| Description | Hardness range (mg/L as <br> $\left.\mathrm{CaCO}_{3}\right)$ |
| :--- | :---: |
| Soft | $0-75$ |
| Moderately hard | $75-100$ |
| Hard | $100-300$ |
| Very hard | $>300$ |

## TYPES OF <br> HARDNESS

- Carbonate Hardness is because of presence of
- $\mathrm{HCO}_{3}-$ and $\mathrm{CO}_{3}{ }^{2-}$ of $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$; Carbonate hardness is also known as temporary hardness as it can be removed by boiling
- Whereas Non Carbonate Hardness is associated with
- Cl - and $\mathrm{SO}_{4}{ }^{2-}$ of $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$
- And is often termed as Permanent Hardness


## WATER

## SOFTENING

- Water softening or reduction of hardness is generally accomplished through Chemical Precipitation or Ion Exchange Process.
- Chemical precipitation is accomplished by converting calcium hardness to Calcium Carbonate and magnesium hardness to magnesium hydroxide.
- This is generally practiced either by Lime Soda ash process or by the Caustic Soda Process.
- Lime Soda ash process is generally preferred.


## LIME SODA PROCESS

- Chemical precipitation is one of the more common methods used to soften water.
- Chemicals normally used are lime (calcium hydroxide, $\mathrm{Ca}(\mathrm{OH})_{2}$ ) and soda ash (sodium carbonate, $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ).
- Lime is used to remove chemicals that cause carbonate hardness. Soda ash is used to remove chemicals that cause non-carbonate hardness.
- When lime and soda ash are added, hardness-causing minerals form nearly insoluble precipitates. Calcium hardness is precipitated as calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$. Magnesium hardness is precipitated as magnesium hydroxide $\left(\mathrm{Mg}(\mathrm{OH})_{2}\right)$.
- These precipitates are then removed by conventional processes of coagulation/flocculation, sedimentation, and filtration. Because precipitates are very slightly soluble, some hardness remains in the water--usually about 50 to 85 $\mathrm{mg} / \mathrm{l}\left(\mathrm{as} \mathrm{CaCO}_{3}\right)$.


## EQUATIONS INVOLVED IN LIME SODA PROCESS

LIME ADDITION

| $\frac{\text { Hardness }}{\mathrm{CO}_{2}}$ | $+\frac{\text { Lime }}{\mathrm{Ca}(\mathrm{OH})_{2}}$ | $\rightarrow$ | $\frac{\text { Precipitate }}{\mathrm{CaCO}_{3}+\mathrm{H}_{2} \mathrm{O}}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Ca}\left(\mathrm{HCO}_{3}\right)_{2}$ | $+\mathrm{Ca}(\mathrm{OH})_{2}$ | $\rightarrow$ | $2 \mathrm{CaCO}_{3}+2 \mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{Mg}\left(\mathrm{HCO}_{3}\right)_{2}$ | $+\mathrm{Ca}(0 \mathrm{OH})_{2}$ | $\rightarrow$ | $\mathrm{CaCO}_{3}+\mathrm{MgCO}_{3}+2 \mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{MgCO}_{3}$ | $+\mathrm{Ca}(\mathrm{OH})_{2}$ | $\rightarrow$ | $\mathrm{CaCO}_{3}+\mathrm{Mg}(\mathrm{OH})_{2}$ |

LIME AND SODA ASH ADDITION

| $\mathrm{MgSO}_{4}$ | $+\frac{\text { Lime }}{\mathrm{Ca}(\mathrm{OH})_{2}} \rightarrow \frac{\mathrm{Mg}(\mathrm{OH})_{2}}{}+\mathrm{CaSO}_{4}$ |
| :--- | :--- | :--- |
| $\mathrm{CaSO}_{4}$ | $+\frac{\text { Soda ash }}{\mathrm{Na}_{2} \mathrm{CO}_{3}} \rightarrow \frac{\text { Precipitate }}{\mathrm{CaCO}_{3}}+\mathrm{Na}_{2} \mathrm{SO}_{4}$ |

- For each molecule of calcium bicarbonate hardness removed, one molecule of lime is used. For each molecule of magnesium bicarbonate hardness removed, two molecules of lime are used. For each molecule of non-carbonate calcium hardness removed, one molecule of soda ash is used. For each molecule of noncarbonate magnesium hardness removed one molecule of lime plus one molecule of soda ash is used.
- $\mathrm{CO}_{2}$ does not contribute to the hardness, but it reacts with the lime, and therefore uses up some lime before the lime can start removing the hardness.


## LIME SODA <br> PROCESS

- To precipitate $\mathrm{CaCO}_{3}$ we need to raise the pH to 10.3 by the addition of Lime $\left[\mathrm{Ca}(\mathrm{OH})_{2}\right.$ ]. The addition of the $\mathrm{OH}^{-}$will convert $\mathrm{HCO}_{3}^{-}$to $\mathrm{CO}_{3}{ }^{2-}$
- To precipitate $\mathrm{Mg}(\mathrm{OH})_{2}$ we need to raise the pH to 11 by the addition of Soda ash [ $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ]. This will add the $\mathrm{CO}_{3}{ }^{2-}$ ion needed to react with the remaining $\mathrm{Ca}^{2+}$
- Some of the added lime $\left[\mathrm{Ca}(\mathrm{OH})_{2}\right]$ is consumed to remove $\mathrm{CO}_{2}$ which is necessary to raise the pH .
- Lime-Soda softening cannot produce a water completely free of hardness because of the solubility of CaCO 3 and $\mathrm{Mg}(\mathrm{OH}) 2$, limitations of mixing and reaction time.
- Thus, the minimum calcium hardness that can be achieved is $30 \mathrm{mg} / \mathrm{L}$ as CaCO 3 , the minimum Magnesium hardness that can be achieved is $10 \mathrm{mg} / \mathrm{L}$ as CaCO , this gives a minimum hardness of $40 \mathrm{mg} / \mathrm{L}$ as CaCO .
- However, treatment is done to provide a water with a hardness in the range of 75 to $120 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$


## EXCESS LIME

- An Excess lime beyond the stoichiometric amount is usually added to
- remove $\mathrm{Mg}^{2+}$ hardness. The minimum excess lime is usually $20 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$, maximum excess lime is $62.5 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}(1.25$ meq/L).
- $\mathrm{Mg}^{2+}$ in excess of $40 \mathrm{mg} / \mathrm{L}^{2 s} \mathrm{CaCO}_{3}$ is not desired as it forms scale in
- water heaters. $\mathrm{Mg}^{2+}$ is expensive to remove, so we only remove $\mathrm{Mg}^{2+}$
- in excess of $40 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$.
- Excess lime ( $1.25 \mathrm{meq} / \mathrm{L}$ ) is added to raise the pH so that precipitation of $\mathrm{CaCO}_{3}$ and $\mathrm{Mg}(\mathrm{OH})_{2}$ takes place.


## - CONVENTIONAL LIME-SODA ASH TREATMENT

- When water has minimal magnesium hardness, only calcium needs to be removed. Only enough lime and soda ash are added to water to raise pH to between 10.3 and 10.6 , and calcium hardness will be removed from the water (but minimal magnesium hardness will be removed).


## - EXCESS LIME TREATMENT

- When magnesium hardness is more than about $40 \mathrm{mg} / \mathrm{l}$ as CaCO 3 , magnesium hydroxide scale deposits in household hot-water heaters operated at normal temperatures of 140 to $150^{\circ} \mathrm{F}$. To reduce magnesium hardness, more lime must be added to the water. Extra lime will raise pH above 10.6 to help magnesium hydroxide precipitate out of the water.


## - SPLIT TREATMENT

- When water contains high amounts of magnesium hardness, split treatment may be used. Approximately 80 percent of the water is treated with excess lime to remove magnesium at a pH above 11, after which it is blended with 20 percent of the source water. Split treatment can reduce the amount of carbon dioxide required to re-carbonate the water as well as offer a savings in lime feed.


## TENTATIVE TREATMENT SCHEME



## RECARBONAT ION



- After adding lime and/or soda ash, treated water will generally have a pH greater than 10 .
- It is necessary to lower the pH to stabilize the water and prevent deposition of carbonate scale on filter sand and distribution piping.
- Recarbonation is the most common process used to reduce pH .
- This procedure adds carbon dioxide to water after softening. Generally, enough carbon dioxide is added to reduce the pH of the water to less than 8.7


## RECARBONATION

- The amount of carbon dioxide added is determined using a saturation index. The Langelier Index (LI) is the most common stabilization index used, but some plants instead use the Rizner Index, (reciprocal of the Langelier Index).
- The Langelier Index is expressed as pH of stabilization ( pHs ) minus actual pH measured ( $\mathrm{pHs}-\mathrm{pH}$ ).
- Langelier Index (L.I.) $=\mathrm{pH}_{\mathrm{s}}-\mathrm{pH}$
- When the Langelier Index is positive, scaling would occur in pipes whereas corrosion would be promoted if langelier indiex in neagtive


## EXAMP

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- Water defined by following analysis to be softened by excess lime and soda ash treatment
- (i) Sketch meq/L bar diagram
- (ii) Calculate the amount of chemicals required for the treatment of 5 MLD of water assuming purity of lime as $70 \%$ and that of soda ash as $80 \%$.
- (iii) Draw a meq/L bar graph for the softened water after recarbonation and filtration, assuming that $80 \%$ of the alkalinity is in the bicarbonate form
- $\mathrm{Ca}^{2}=40 \mathrm{mg} / \mathrm{L} ; \mathrm{Mg}^{2+}=18 \mathrm{mg} / \mathrm{L}, \mathrm{CO}_{2}=8.8 \mathrm{mg} / \mathrm{L} ; \mathrm{Na}^{+}=20 \mathrm{mg} / \mathrm{L}$
- $\mathrm{HCO}_{3}=135 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3} ; \mathrm{SO}_{4}=30 \mathrm{mg} / \mathrm{L} ; \mathrm{Cl}=35 \mathrm{mg} / \mathrm{L}$


## SOLUTI <br> ON

- Convert concentration of ions to meq/L
- $\mathrm{Ca}^{2+}=40 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{meq} / 20 \mathrm{mg}=2.0 \mathrm{meq} / \mathrm{L}$
- $\mathrm{Mg}^{2+}=18 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{meq} / 12 \mathrm{mg}=1.5 \mathrm{meq} / \mathrm{L}$
- $\mathrm{Na}^{+}=20 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{meq} / 23 \mathrm{mg}=0.87 \mathrm{meq} / \mathrm{L}$
- $\mathrm{HCO}_{3}{ }^{-}=135 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{meq} / 50 \mathrm{mg}=2.7 \mathrm{meq} / \mathrm{L}$
- $\mathrm{SO}_{4}{ }^{2-}=30 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{meq} / 48 \mathrm{mg}=0.625 \mathrm{meq} / \mathrm{L}$
- $\mathrm{Cl}^{-}=35 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{meq} / 35.5 \mathrm{mg} \sim 1.0 \mathrm{meq} / \mathrm{L}$
- $\mathrm{CO}_{2}=8.8 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{meq} / 22 \mathrm{mg}=0.4 \mathrm{meq} / \mathrm{L}$
- meq/L Bar Diagram of Raw Water

- Possible Hypothetical Hardness Causing Species
- $\mathrm{Ca}\left(\mathrm{HCO}_{3}^{-}\right)_{2}=2.0 \mathrm{meq} / \mathrm{L} ; \mathrm{Mg}\left(\mathrm{HCO}_{3}^{-}\right)_{2}=0.7 \mathrm{meq} / \mathrm{L}$;
- $\mathrm{MgSO}_{4}{ }^{2-}=0.625 \mathrm{meq} / \mathrm{L} ; \mathrm{MgCl}_{2}=0.175 \mathrm{meq} / \mathrm{L}$


## CHEMICALREQUREM ENTS

- Chemical Requirement

| Species | Lime $(\mathrm{meq} / \mathrm{L})$ | Soda $(\mathrm{meq} / \mathrm{L})$ |
| :--- | :--- | :--- |
| $\mathrm{Ca}\left(\mathrm{HCO}_{3} \overline{\mathrm{O}}_{2}\right.$ | 2.0 | --- |
| $\mathrm{Mg}\left(\mathrm{HCO}_{3} \overline{\mathrm{O}}_{2}\right.$ | 1.4 | --- |
| $\mathrm{MgSO}_{4}{ }^{2-}$ | 0.625 | 0.625 |
| $\mathrm{MgCl}_{2}$ | 0.175 | 0.175 |
| Excess Lime | 1.25 |  |

- Total Lime $=5.45 \mathrm{meq} / \mathrm{L}$
- Commercially CaO is used its equivalent weight is 28
- Lime Required $=5.45 \mathrm{meq} / \mathrm{L} \times 28 \mathrm{mg} / \mathrm{meq} \times 5000000 \mathrm{~L} / \mathrm{d}$
- $\quad=763 \mathrm{Kg} / \mathrm{d}$; purity of commercial lime is

70\%

- Actual Lime Requirement $=763 / 0.7=1090 \mathrm{Kg} / \mathrm{d}$
- Soda Ash Requirement $=0.8$ meq/L
- Equivalent weight of $\mathrm{Na}_{2} \mathrm{CO}_{3}=53 \mathrm{~g}$
- Total Soda Ash Requirement
$\cdot=0.8 \mathrm{meq} / \mathrm{L} \times 53 \mathrm{mg} / \mathrm{meq} \times 5000000 \mathrm{~L} / \mathrm{d} \times 1 / 0.8$ (purity is 80\%)
- $=265 \mathrm{Kg} / \mathrm{d}$.


## BAR DIAGRAM OF FINISHED WATER

- Bar diagram of finished water after Recarbonation assuming $80 \%$ of alkalinity as $\mathrm{HCO}_{3}$ - and hardness of finished water consisting of 30 $\mathrm{mg} / \mathrm{L}$ of $\mathrm{Ca}^{2+}$ hardness and $10 \mathrm{mg} / \mathrm{L}$ of $\mathrm{Mg}^{2+}$ hardness


