LIME-SODA ASH SOFTENING

It is necessary to remove certain chemicals from water and waste water

Water: Iron and Maganese
Arsenic
Hardness
Nitrate
Organic chemicals

Industrial wastewater: virtually any chemical, but especially metals organic chemicals.

Hardness

A water is “hard” if

1. Soap does not easily form a foam or lather.
2. the water leaves scale in hot water pipes, boilers, etc.

Hardness arises from divalent metal ions in the water

Ca^{+2}, Mg^{+2}, Sr^{+2}, Fe^{+2}, Mn^{+2} comes from natural rocks in source area, especially limestone

eg. Calcite $CaCO_3$, Dolomite $CaMg(NO_3)_2$

Different definitions of hardness

$$\text{Total hardness} = \sum[M^{+2}] \quad X \quad 50 / \text{eq. wt. of } M^{+2}$$

Hardness is expressed in equivalents of $CaCO_3$

Ca - Mw = 40 X 1 = 40
C - Mw = 12 X 1 = 12
O - Mw = 16 X 3 = 48
100 = MW

Since Ca^{+2} and CO_3^{2-} have valence of 2
Equivalent weight of $CaCO_3$ = 100/2 = 50

CO_2 = 8.8 mg/L as CO_2
Alk (HCO_3^-) = 115 mg/L as $CaCO_3$
Ca^{+2} = 70 mg/L
Mg^{+2} = 9.7 mg/L
Na^+ = 6.9 mg/L

SO_4^{2-} = 96 mg/L
Cl^- = 10.6 mg/L

M^{++}	Concn.in (mg/L)	Mw	Eq. Wt.	Hardness
Ca^{+2}	70	40	20	175
Mg^{+2}	9.7	244	12.2	39.8
				214.8

pretty hard water!!!

Most hardness is due to Ca and Mg

Ca hardness = that due to Ca

Mg hardness = that due to Mg

Total hardness = Ca hardness + Mg hardness

Carbonate hardness = part of total hardness equivalent to carbonate plus bicarbonate alkalinity.

Refresher on alkalinity
[Alk] = Capacity for solutes to neutralize a strong acid.

$$= \sum[\text{strong bases}] \quad - \quad \sum[\text{strong acids}$$

Strong acids are those that completely dissociate in water : HCl, H_2SO_4, HNO_3, HBr

Strong bases completely dissociatess :NaOH, KOH, $Ca(OH)_2$, LiOH, RbOH, $Sr(OH)_2$

$$[Alk] = [Na^+] + [K^+] + 2[Ca^{+2}] + 2[Mg^{+2}] - [Cl^-] - 2[SO_4^{2-}] - [NO^{3-}]$$

$$= \sum[\text{strong bases}] - \sum[\text{strong acids}]$$

Can also find charge balance assuming carbonates dominate system.

$$\sum[SB] + H^+ = \sum [SA] + [OH^-] + 2[CO_3^{2-}] + [HCO_3^-]$$

$$\sum[SB] - \sum [SA] = [Alk] = [OH^-] - [H^+] + 2[CO_3^{2-}] + [HCO_3^-]$$

Carbonate hardness (for [Alk] in terms of $CaCO_3$)

If [Alk] $<$ total hardness then carbonate hardness =[Alk]

If [Alk] $>$ total hardness then carbonate hardness = total hardness

Carbonate hardness causes scaling at high temperatures

$$Ca^{+2} + HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

Non carbonate hardness = total hardness - carbonate hardness

For water treatment, carbonate hardness is removed by adding

lime $Ca(OH)_2$

First lime react with any CO_2:

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

Then lime reacts to remove carbonate hardness

2. $Ca^{+2} + HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3 + 2\,H_2O$
3. $Mg^{+2} + 2HCO_3^- + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(CO_3)_2 + 2H_2O$

And finally to remove non carbonate Mg hardness

4. $Mg^{+2} + SO_4^{2-} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{+2} + SO_4^{2-}$

5. $Mg^{+2} + 2Cl^- + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{+2} + 2Cl^-$

Reaction 4 and 5 simply swap Mg non carbonate hardness for Ca non carbonate hardness

Reaction 1-5 remove magnesium hardness and calcium carbonate hardness. Calcium non

carbonate hardness in original solution plus that created removing Mg hardness remain.

For water low in Mg and with carbonate Ca hardness, this would be sufficient treatment

called “Single- stage lime treatment” , “single stage softening” or “ undersoftening”.

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

7. $CO_3^{2-} + CO_2 + H_2O \rightarrow 2HCO_3^-$

Recarbonation is also done to ‘stabilize’ the water

If water is supersaturated with $CaCO_3$, it will precipitate as ‘scale’
If water is undersaturated , water can be ‘ aggressive’ and cause ‘pipe corrosion.
Ideal is to keep water slightly oversaturated to maintain thin protective coat of CaCO3
on inside of pipe.
Scale precipitation involves the chemical reactions:

Typical process in water treatment plant.

$CaCO_3$ added in ‘flash mixer’

Water/lime mix goes into flocculator, then clarifier to precipitate and remove $CaCO_3$
(Tr = 1-2 hours).

Water is then ‘recarbonated’
Recarbonation is needed because ddition of $Ca(OH)_2$ raises pH of water to 10.2 to 10.5

Recarbonation consists of bubbling CO_2 through treated water , lowering pH to 8.7 to 9.0

$$Ca^{+2} + CO_3^{2-} \rightleftharpoons CaCO_3(s) \qquad 1/K_s$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2$$

$$Ks = \frac{[Ca^{+2}]\,[CO_3^{2-}]}{[CaCO_3(s)]}$$

$$K_2 = \frac{[CO_3^{2-}]\,[H^+]}{[HCO_3^-]}$$

Overall reaction $Ca^{+2} + HCO_3^- \rightleftharpoons CaCO_3(s) + H^+$

$$K = \frac{[Ca^{+2}]\,[HCO_3^-]}{[H^+]} = \frac{K_s}{K_2}$$

Rearrange it to get $[H^+] = \dfrac{[Ca^{+2}]\,[HCO_3^-]}{K}$

$$[H^+] = \frac{[Ca^{+2}][HCO_3^-]}{K}$$

$$\log[H^+] = \log[Ca^{+2}] + \log[HCO_3^-] - \log K$$
$$-\log[H^+] = -\log[Ca^{+2}] - \log[HCO_3^-] + \log K$$

$$pH = pCa + pHCO_3^- + \log \frac{K_s}{K_2}$$
$$= pCa + p[Alk] + \log \frac{K_s}{K_2}$$

$I = pH_{actual} - pH_{eq} = SI$ = Langlier stability Index

$I > 0 \rightarrow CaCO_3$ precipitates

$I = 0 \rightarrow$ Stable

$I < 0 \rightarrow CaCO_3$ dissolve

$I = 0.2$ is desirable – carbonation steps seeks to set I approxly 0.2

K_2, K_s are function of temperature.

$pK_s = 8.4$ $pK_2 = 10.4$ at $T = 15C$

Conventional lime treatment process looks like

Water → Lime → Coagulation → Sedimentation → Recarbonization → Filteration

LIME-SODA ASH SOFTENING
PART-2

For waters with non- carbonate hardness, single stage softening is sufficient. Leftover

Hardness is removed by addition of soda ash. (Na_2CO_3).

8. $Ca^{+2} + SO_4^{2-} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+ + SO_4^{2-}$

9. $Ca^{+2} + Cl^- + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+ + Cl^-$

Practical limits of lime- soda ash softening are dictated by solubility of precipitates

Ca = 30g/L as $CaCO_3$

Mg = 10 g/L as $MgCO_3$

In practice, residual hardness = 50 to 80 mg/L

This water has high pH and needs to be recarbonated.

Lime soda ash treatment is usually treated by " two –stage softening" also called " excess lime treatment.

Split treatment is similar, except only part of water is treated with lime. Other part by passes lime treatment and soda-ash treatment along with lime treated water.

The CO_2 in untreated water neutralizes high pH in lime treated water and recarbonization is not needed.

Water split is computed such that enough Mg is removed in lime treated water to meet target Mg level in combined finished water.

Example. If a waste water has the following constituents, calculate total, carbonate, non-carbonate -hardness.

CO_2 = 8.8mg/L Alk = 115mg/L as $CaCO_3$
Ca^{+2} = 70mg/L SO_4^{2-} = 96mg/L
Mg^{+2} = 9.7mg/L Cl^- = 10.6mg/L
Na^+ = 6.9mg/L

Easiest method is to construct a table that converts all concentrations to equivalent concentrations and then to equivalents of $CaCO_3$.

	conc. (mg/L)	Mw	Equiv. (eq/molecules)	Eq. Wt. (gm/mole eq.)	[M] eq/L	mg/L as $CaCO_3$
CO_2	8.8	44.0	2	22.0	0.40	20.0
Ca^{+2}	70	40.0	2	20.0	3.5	175
Na^+	6.9	23.0	1	23.0	0.30	15.0
Mg^{+2}	9.7	24.4	2	12.2	0.80	39.8
					4.60	229.8
Alk	115	100	2	50.0	2.3	115.0
SO_4^{2-}	96	96.0	2	48.0	2.0	100.0
Cl^-	10.6	35.5	1	35.5	0.30	14.9
					4.60	229.9

Total hardness = Ca^{+2} + Mg^{+2} = 175 + 39.8 = 214.8 mg/L

Carbonate hardness = [Alk] = 115mg/L as $CaCO_3$

Non carbonate hardness = TH –CH = 99.8mg/L as $CaCO_3$

Mg non carbonate hardness = 39.8mg/L as $CaCO_3$

Lime required

For CO_2	=	20.0 mg/L as $CaCO_3$
For carbonate hardness	=	115.0
For Mg non carbonate hardness	=	39.8
		174.8 mg/L as CaCO3

Convert from $CaCO_3$ to CaO

$CaO/CaCO_3$ = 40+ 16/40+ 12+3X16 = 56/100 = 28/50

174.8 mg/L as $CaCO_3$ = 97.9 mg/L as CaO.
Include excess lime of 35mg/L
Required lime = 133 mg/L

Soda ash for non carbonate hardness

NCH = 99.8 mg/L as $CaCO_3$ (2.0meq)

(recall that Mg NCH was treated with lime but simply swaps Ca for Mg, so still needs treatment with soda ash)

Required soda ash = 99.8 mg/L as $CaCO_3$

Convert to Na_2CO_3

$$\frac{Na_2CO_3}{CaCO_3} = \frac{2X23 + 12 + 3X16}{40+12+3X16} = 1.06$$

Required soda ash = 1.06X 99.8 = 106mg/L