# *Engineering Training*

### 3.1    Influent Cold Lime Softening

Plants A, B, C and D use another method of clarification called lime softening. Lime softeners have several functions: remove suspended solids, remove iron, remove some silica, remove some carbonate hardness, and remove some carbonate alkalinity. The removal of suspended solids is a clarification process as described in the previous section.

The removal of iron occurs in lime softeners because the high pH causes the iron to convert to a less soluble species, iron hydroxide (FeOH), and precipitates onto the calcium carbonate sludge.  Silica removal occurs in a different manner; silica adheres or "sticks" to the sludge.

The removal of carbonate hardness ($CaCO_3$, $MgCO_3$, $BaCO_3$, $SrCO_3$) is a softening process. Carbonate hardness consists of the calcium ($Ca^{++}$), magnesium ($Mg^{++}$), barium ($Ba^{++}$) and strontium ($Sr^{++}$) cations that are associated with carbonate anions ($CO_3^{=}$). The concentrations of barium and strontium carbonates are very low in surface water and are assumed to be zero. Therefore, the carbonate hardness equals the sum of the concentrations of calcium carbonate and magnesium carbonate. Most raw waters contain both carbonate hardness and non-carbonate hardness. Non-carbonate hardness is the calcium and magnesium cations associated with sulfate ($SO_4^{=}$) and chloride ($Cl^-$) anions.

Removing carbonate hardness in the lime softener reduces the load on the downstream sodium zeolite softeners, demineralizers or reverse osmosis units for boiler feedwater. For cooling tower make-up, the lower hardness concentration may be an advantage, allowing an increase in the cycles of concentration but the disadvantage is the risk of post-precipitation of lime.

Alkalinity removal is described in **Section 3.2.2 Chemicals (purpose & function)**.

The lime softening reaction is relatively slow, and will continue downstream of the clarifier, exceeding the solubility of calcium carbonate in the clarified water. This phenomenon is not carryover; it is post-precipitation. The precipitated calcium carbonate can accumulate on the surface of media filters, causing high pressure differentials.  It can form scale on the surface of the transfer pipes, reducing the cross-sectional area and ultimately starving the plant of clarified and filtered water. In extreme cases, the post-precipitation occurs in the heat exchangers. This process takes several decades to occur, and, although reversible, must be reversed slowly to avoid large particles of scale causing additional problems from a "too-aggressive" dissolution program (e. g. overfeed of acid). In contrast to the slow accumulation of scale due to post-precipitation, carryover is usually the cause of rapid calcium carbonate fouling.

Plants A and B inject sulfuric acid at the effluent of the lime softener to increase the solubility of the calcium hydroxide and calcium carbonate and prevent this post-precipitation reaction. The pH target for this practice is that which is required to maintain a Langelier Saturation Index nearly equal to zero; e. g. a condition that is neither scale-forming nor scale-dissolving (corrosive). Operators cannot determine the degree of post precipitation visually; they should measure the acidified and non-acidified hardness (e. g. add an aliquot of acid to the sample prior to the hardness test).  If the two measurements are equal, then there is no precipitated calcium carbonate or calcium hydroxide in the sample.

### 3.1.1   Basic Design Engineering and Operating Criteria

Engineers often refer to the clarifier by the manufacturer; B and C have Graver Reactivators (sludge recirculation units) while A has one Eimco Reactivator and one Permutit sludge blanket unit, while D has a unit similar to the design of the Eimco Reactivator (**Figure 3-7**). The Graver units at C are no longer operated as lime softening units; Corporate replaced the lime with an iron-based coagulant polymer to improve the cooling water chemistry and the downstream RO reliability.
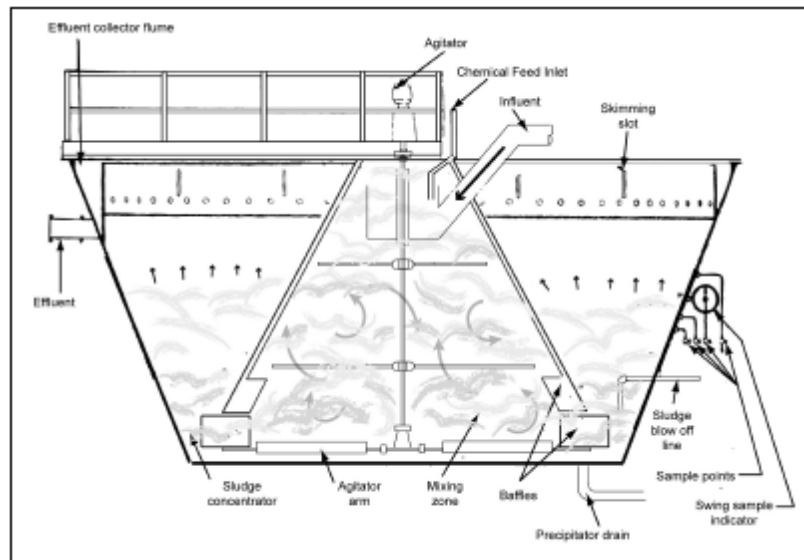
**Figure 3-7 – Sludge Blanket Clarifier (*courtesy of Siemens*)**

Lime softening clarifiers have the same operating limitations as conventional clarifiers. Corporate specifies that the key design parameter, rise rate, be a maximum of 1.0 gpm/ft$^2$. Operators should purge the lime solids from the vessel prior to unit shutdown to avoid forming a dense, compacted lime bed that may over-torque the rake motor, damaging the unit.

Similar to clarifiers treated with polymer, lime softeners operate best at steady flowrates. The clarified water storage tank should have a large enough dead band to accommodate the dynamically changing demand for clarified water while allowing the lime softener to operate at steady state. Operating clarifiers above their rated flowrate will cause poor results. Often clarifiers can be modified to operate at higher flowrates by installing floc barriers. Similarly, if the plant has modified the clarifier without studying the effect on the system performance, the clarifier may not be able to perform at the maximum rated capacity.

### 3.1.2   Chemicals (purpose & function)

Lime softeners use lime (CaO or Ca(OH)$_2$) or lime and sodium aluminate (Na$_2$Al$_2$O$_4$) to remove hardness by precipitation and suspended solids by coagulation and flocculation. In simple terms, feeding a calcium-based chemical, lime, increases the calcium carbonate concentration above the maximum solubility limit, forcing precipitation of calcium carbonate.

Alkalinity that naturally occurs in raw water is an important part of the lime softening reaction. Everyone is familiar with alkalinity; in some areas of the U. S., the water "feels slippery," making it difficult to determine if you have completely rem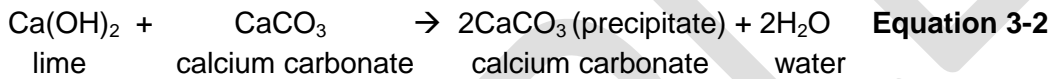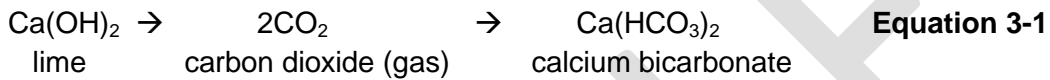oved the soap residue from your skin. Alkalinity is the acid-neutralizing power of an aqueous solution with respect to bicarbonate (HCO$_3^-$), carbonate (CO$_3^=$) and hydroxide (OH$^-$) alkalinity. These three different alkalinity measurements are identified by the first letter of the name of the indicator dye used in the laboratory test, as shown in **Table 3-1**. M Alkalinity is sometimes called Total Alkalinity because it measures all species of carbonates and hydroxides.

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**Table 3-1 – Alkalinity Measurements**

| Alkalinity Measurement | Carbonate Species |
|---|---|
| P Alkalinity | All hydroxides, ½ carbonates |
| M Alkalinity (Total Alkalinity) | All bicarbonates, all carbonates, all hydroxides |
| O or OH Alkalinity | All hydroxides |

Adding lime to water that contains bicarbonate hardness results in the formation of calcium bicarbonate ($Ca(HCO_3)_2$) (**Equation 3-1**) followed by the formation of calcium carbonate ($CaCO_3$) (**Equation 3-2**).

$$Ca(OH)_2 \rightarrow \quad 2CO_2 \quad \rightarrow \quad Ca(HCO_3)_2 \qquad \textbf{Equation 3-1}$$
$$\text{lime} \qquad \text{carbon dioxide (gas)} \qquad \text{calcium bicarbonate}$$

$$Ca(OH)_2 + \quad CaCO_3 \quad \rightarrow 2CaCO_3 \text{ (precipitate)} + 2H_2O \quad \textbf{Equation 3-2}$$
$$\text{lime} \qquad \text{calcium carbonate} \qquad \text{calcium carbonate} \qquad \text{water}$$

As shown in **Table 3-2**, calcium carbonate is very insoluble; it precipitates, removing calcium hardness and carbonate alkalinity from the water. **Figure 3-8** shows the equilibrium between carbonic acid, bicarbonate and carbonate as a function of pH.

**Table 3-2 Solubility of Calcium Carbonate and Calcium Bicarbonate as a f(temperature)**

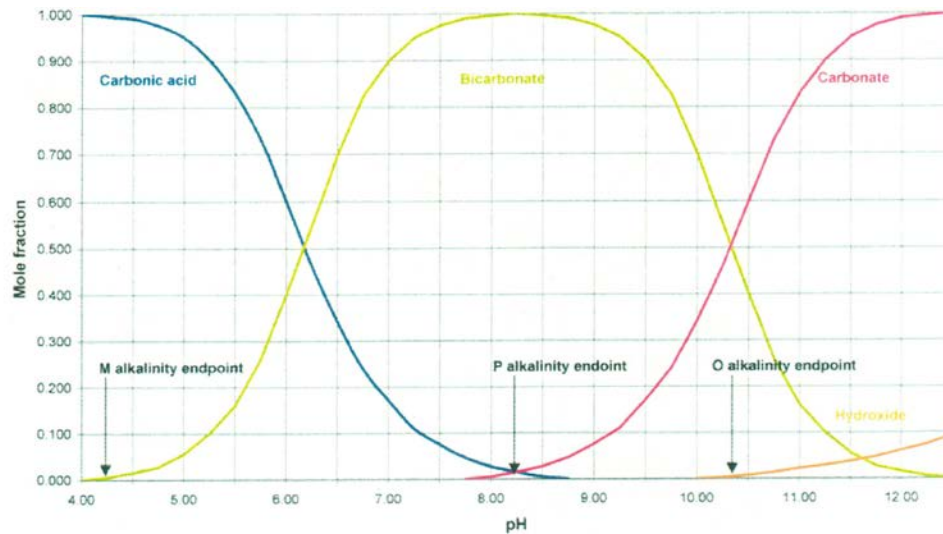| Substance | Formula | 0 °C | 10 °C | 20 °C | 30 °C | 40 °C | 50 °C | 60 °C | 70 °C | 80 °C | 90 °C | 100 °C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Calcium bicarbonate | $Ca(HCO_3)_2$ | 16.1 | | 16.6 | | 17.1 | | 17.5 | | 17.9 | | 18.4 |
| Calcium carbonate (Aragonite) | $CaCO_3$-Aragonite | | | 0.0007753 | | | | | | | | |
| Calcium carbonate (Calcite) | $CaCO_3$-Calcite | | | 0.0006170 | | | | | | | | |

**Figure 3-8 – Carbonate Alkalinity Equilibrium (Courtesy of MarTech Systems, Inc. Company)**

If the raw water has only carbonate hardness, and no non-carbonate hardness, then the effluent calcium hardness would be 35 ppm. However, most surface water contains non-carbonate hardness, a contaminant that is unaffected by the lime softening reaction. Therefore, the minimum effluent calcium hardness would be the sum of the non-carbonate calcium hardness and 35 ppm as $CaCO_3$.

Plant C removes magnesium cations by feeding sodium hydroxide (caustic) in conjunction with the lime. Silica will adsorb on the precipitated magnesium: one ppm of silica co-precipitates with every 70 ppm of magnesium. The practical calcium solubility limit is 35 ppm as $CaCO_3$ and the practical magnesium solubility limit is 75 ppm as $CaCO_3$ using cold lime-soda treatment.

### 3.1.3 KPI/KOI Specifications

The most important KOI for lime softeners is OH alkalinity as measured in the clearwell. Operators do not measure OH alkalinity directly; rather they measure P and M alkalinity through titration tests and calculate the OH alkalinity (**Equation 3-3**).

OH alkalinity = (2 x P) – M          **Equation 3-3**

C uses a 2P-M specification range of 0 to +10 as $CaCO_3$ while B uses a 2P-M specification range of +5 to +15 ppm as $CaCO_3$. Controlling the OH alkalinity is critical to optimal removal of carbonate hardness, the proper concentration of alkalinity in the boiler make-up water, and minimizing the risk of post-precipitation of calcium carbonate. The second most important performance metric for lime softeners is the effluent turbidity; Corporate specifies a maximum of 3 NTU. Clarifier manufacturers will specify a maximum effluent turbidity of 3 NTU for lime softeners as recently demonstrated on the GME project; thus, with steady state operation and good blowdown control, operators should be able to meet the Corporate specification. Other KOI measurements for the clarifier effluent include total hardness, calcium hardness, magnesium hardness, silica, pH and turbidity.

Operators measure the lime softener effluent quality three times per day. Some plants have on-line turbidity analyzers; these units require simple daily cleaning. Operators make adjustments

in the coagulant feed rate when the raw water turbidity changes. Raw water turbidity changes due to local storms or drought or weather events upriver such as rain or snowmelt.

The boiler section describes how carbonate alkalinity in the boiler make-up water concentrates in the boiler and thermally degrades, forming carbon dioxide gas that leaves the boiler with the steam. As the steam condenses and forms condensate, the carbon dioxide converts back to carbonic acid, lowering the pH and increasing the corrosion rate in the condensate system. Plant personnel feed neutralizing amine to counteract the negative effects of carbonic acid in the condensate. The higher the concentration of OH alkalinity, the lower the concentration of carbonate alkalinity in the boiler make-up, the boiler water and the condensate.

### 3.1.4   Lessons Learned Case History – lime softeners

***Background –*** B has two cold lime softeners that supply water to the cooling water circuit and the boiler pretreatment system.

***Event –*** Since being commissioned in approximately 1980, the B refinery has not fed sulfuric acid to control post-precipitation. Although the post-precipitation reaction occurs slowly, it will eventually accumulate solids on the walls of the transfer piping, permanently restricting flow. The effects of post-precipitation affect small-diameter lines first, choking pressure taps and sample lines for on-line instruments. **Figure 3-9** shows an accumulation of scale on the six-inch blowdown piping from the cooling tower.

***Lesson Learned –*** Post-precipitation is unavoidable in distribution systems for cold lime softeners, even in warm climates such as B's location. Feeding acid or carbon dioxide is essential to prevent post-precipitation. Prevention of post-precipitation is the only reliable method; it is difficult and potentially dangerous to dissolve accumulated scale by feeding high concentrations of acid while the cooling circuit is operating.



**Figure 3-9 – Accumulation of Post-precipitation Scale on Cooling Tower Blowdown Line**