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Cold Lime Softening

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Content

1. Cold Lime Softening

Cold lime softening, also referred to as Clark's process, is a treatment method to reduce raw water hardness, silica, alkalinity, and other constituents. The lime softening process is commonly used to prepare water for use as cooling tower makeup, or as a first-stage treatment to be followed by ion exchange or reverse osmosis processes. The water is treated with lime or a combination of lime and soda ash (carbonate ion). These chemicals react with the hardness and natural alkalinity in the water to form insoluble compounds. The compounds precipitate and are removed from the water by sedimentation/clarification. Waters with moderate to high hardness and alkalinity concentrations (150-500 ppm as $CaCO_3$) are often treated in this method.

2. Chemistry of Cold Lime Softening

Text In most raw water supply, hardness is present as calcium and magnesium bicarbonate, often referred to as carbonate hardness or temporary hardness. These compounds result from the action of acidic, carbon dioxide laden rainwater on naturally occurring minerals in the earth, such as limestone. For example:

- $CO_2 + H_2O = H_2CO_3$
- $H_2CO_3 + CaCO_3$ ¯ $= Ca(HCO_3)_2$

Lime Softening produced at ambient temperatures is referred to as cold lime softening. When hydrated lime, $Ca(OH)_2$, is added to the water being treated, the following reactions occur:

- $CO_2 + Ca(OH)_2 = CaCO_3$ ¯ $+ H_2O$
- $Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3$ ¯ $+ 2H_2O$
- $Mg(HCO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2$ ¯ $+ 2CaCO_3$ ¯ $+ 2H_2O$

When optimal chemical control is maintained on lime feed, the calcium hardness may be reduced to 35-50 ppm. Permanent calcium hardness is not affected by treatment with lime alone. If non carbonate magnesium hardness is present in an amount greater than 70 ppm, and an excess hydroxyl alkalinity of about 5 ppm is maintained, the magnesium can be reduced to about 70 ppm, but the calcium will increase in proportion to the magnesium reduction. For example, in cold lime treatment of a water containing 110 ppm of calcium, 95 ppm of magnesium, and at least 110 ppm of alkalinity (all expressed as calcium carbonate), calcium could theoretically be reduced to 35 ppm and the magnesium to about 70 ppm. However, an additional 25 ppm of calcium would be expected in the treated water due to the following reactions:

- $MgSO4 + Ca(OH)2 = Mg(OH)2\ ^{-} + CaSO4$
- $MgCl2 + Ca(OH)2 = Mg(OH)2\ ^{-} + CaCl2$

To optimize magnesium reduction, which also improves silica reduction in cold process softening, sodium aluminate may be introduced. The sodium aluminate provides hydroxyl ion $(OH-)$ required for improved magnesium reduction, without increasing calcium hardness in the treated water. In addition, the hydrolysis of sodium aluminate results in the formation of aluminum hydroxide, which aids in floc formation, sludge blanket conditioning, and silica reduction. The reactions are as follows:

- $Na2Al2O4 + 4H2O = 2Al(OH)3\ ^{-} + 2NaOH$
- $Mg\ [\ SO4\ ] + 2NaOH = Mg(OH)2^{-} + [\ Na2SO4\ ]$
- $Mg\ [\ Cl2\ ] + 2NaOH = Mg(OH)2^{-} + [\ 2NaCl\ ]$

Soda ash $(Na2CO3)$ is also used to improve hardness reduction. It reacts with non-carbonate calcium hardness according to the following:

- $CaSO4 + Na2CO3 = CaCO3\ ^{-} + Na2SO4$
- $CaCl2 + Na2CO3 = CaCO3\ ^{-} + 2NaCl$

Permanent magnesium hardness reduction in cold process softening requires added lime. The reactions are as follows:

- $MgSO4 + Ca(OH)2 + Na2CO3 = Mg(OH)2\ ^{-} + CaCO3\ ^{-} + Na2SO4$
- $MgCl2 + Ca(OH)2 + Na2CO3 = Mg(OH)2^{-} + CaCO3\ ^{-} + 2NaCl$

In these reactions, dissolved solids (TDS) are not reduced because a solution reaction product (sodium sulfate or sodium chloride) is formed.

3. Treatment of Other Contaminants

Lime softening processes will reduce oxidized iron and manganese to about 0.05 and 0.01 ppm, respectively. Raw water organics (color-contributing colloids) are also reduced. Turbidity may be reduced to about 1.0 NTU with filtration following chemical treatment. Raw water turbidity exceeding 100 NTU may be tolerated in these systems; however, it may be necessary to coagulate raw water solids with polyelectrolyte. Oil may also be removed by adsorption on the precipitates formed during treatment. However, oil in concentrations above about 30 ppm should be reduced before lime treatment because higher concentrations of oil may exert a dispersing influence and cause floc carryover.

4. Typical Equipment Employed

The first cold lime-soda softening was carried out in a "batch" method. An excess of treating chemicals was mixed with the water in a large basin. After approximately 4 hr, the treated water was decanted from the basin, leaving the settled precipitates in the basin.

Today, continuous sludge-contact softeners are used to provide a constant flow with effluent quality superior to that obtained through batch treatment. Treating chemicals are added as a function of flow rate and water quality to the rapid mix zone of the unit. Sludge, recirculated either internally or externally to the unit, may be returned to this rapid mix zone for improved softening, softened water clarity, and silica reduction.

The water then flows to the slow mix zone of the unit. Here, the precipitation reactions continue, and the precipitates formed become large enough to begin settling. In the sludge-contact unit, the water flows through a bed of sludge for additional contact. The sludge level is maintained by the proper combination of sludge bed conditioning chemicals, mechanical agitation, hydraulic suspension, and sludge blowdown. A discernible line of separation between clarified water and slurry pool should exist in a properly operated unit. Effluent turbidity is usually less than 10 NTU.

Flow rate is usually limited to less than 1.5 gpm/ft2 of settling area. A retention time of 1 hr is required to allow the softening reactions to come as close to completion as possible.

Because the reactions in cold process softening are not complete, the water contaminant levels leaving the unit are unstable. With additional time and/or increased temperature, further precipitation will occur downstream of the unit. Frequently, acid or carbon dioxide is added to stabilize the water. The pH is reduced from about 10.2 to between 8.0 and 9.0, which converts the carbonate to the more soluble bicarbonate.

5. Limitations

Given proper consideration of raw water quality and ultimate end use of the treated water, the application of precipitation processes has few limitations. However, operational difficulties may be encountered unless the following factors are controlled:

Temperature	Cold and warm units are subject to carryover if the temperature varies more than 4°F/hr (2°C/hr). Hot process units are less sensitive to slight temperature variations. However, a clogged or improper spray pattern can prevent proper heating of the water, and carryover can result.
Hydraulics	In any system, steady-state operation within design limits optimizes the performance of the equipment. Rapid flow variations can cause severe system upsets. Suitable treated water storage capacity should be incorporated into the total system design to minimize load swings on the softener.
Chemical Control	This should be as precise as possible to prevent poor water quality. Because of the comparatively constant quality of most well waters, changes in chemical feed rates are largely a function of flow only. However, surface water quality may vary hourly. Therefore, for proper control, it is imperative that users perform frequent testing of the raw water as well as the treated effluent and adjust chemical feed accordingly.

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