

Lime Softening

Lime Softening is an operation which has been used for the past 150 years to remove hardness and soften the water. This article will discuss lime softening through a new perspective, instead of going through the detailed chemical equations; we will focus on “practical conclusion” of the reactions. In addition, the term “alkalinity” will deliberately not be brought up, even though traditionally it is part of the chemistry of lime softening. Alkalinity is a “loose” definition of carbonate species’ concentration.

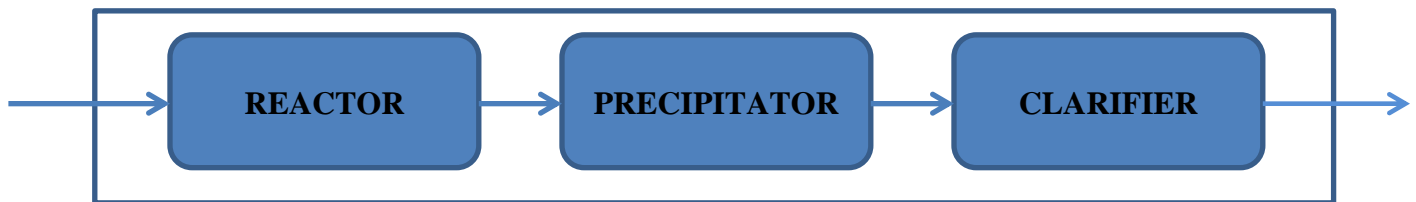
Carbonate—not Alkalinity—is the main player of lime softening chemistry. However alkalinity fails to represent carbonate species’ concentration accurately; especially when pH is either very high or very low. There are also interferences like carboxylic acids in Alkalinity measurement which make it inaccurate.

An old rule of thumb is that lime softening is the method of choice for hardnesses higher than 100-150 mg/L and flowrates larger than 200 m³/h. However, if water is “problematic” (e.g. a high TDS

water) then the cut-off points for hardness and flowrate could be decreased.

Hardness practically, means the summation of calcium and magnesium ions. The concept of lime softening is to remove “hardness-causing” ions by converting them to particles. A lime softener is actually a reactor, a precipitator and a clarifier. All these units together make the lime softener a complicated unit operation. The block flow diagram of a typical lime softener is depicted in Fig – 1.

Fig -1



In the reactor, the hardness ions react with added chemicals which convert them to small suspended solids. In the precipitation section, where precipitation/crystallization is the main process, small particles are promoted mechanically and chemically to cause the bigger particles (generally bigger than 100micron) to settle quickly. Clarifier is the section that provides enough area and

residence time for sedimentation and the generation of clear water.

Therefore, lime softening consists of three separate sections: reaction (which converts hardness to a low solubility salts), precipitation (which happens after oversaturation of water with low soluble salts), and the sedimentation of generated particles.

There are three main types of lime softening systems; Cold Lime Softener (CLS), Warm Lime Softener (WLS), and Hot Lime Softener (HLS). As you may notice, this classification is based on the operating temperature of the system, though there is not a clear and cut distinction between them. The operating temperature range of each system is tabulated in Table – 1.

Table - 1

<i>Lime Softener Type</i>	<i>Operating Temperature</i>
<i>CLS</i>	15 °C - 60 °C
<i>WLS</i>	60 °C - 85 °C
<i>HLS</i>	90 °C - 105 °C

Typical theoretical hardness concentration in lime softener effluent is mentioned in Table – 2.

Table - 2

<i>Lime Softener Type</i>	<i>Residual Hardness</i>
<i>CLS</i>	80-110 mg/L
<i>WLS</i>	30-50 mg/L
<i>HLS</i>	15-25 mg/L

The first invented lime softener was the cold one, CLS, and was used for softening potable water. CLS was very popular until recently when municipalities stopped softening the potable water. WLS and HLS are the versions which are popular in

industrial water treatments. HLS is very popular for treating make up water for high pressure boilers which need very low hardness feed waters. HLS and WLS are used in oil extraction facilities to soften the produced water to prepare boiler feed water for Once

Through Steam Generators (OTSG's), and both generate water with almost the same level of hardness practically. Table-3 shows a summary of differences between WLS and HLS.

Table -3

HLS	WLS
<ul style="list-style-type: none"> • Operating temperature between 90°C to 110 °C • Better hardness removal efficiency (theoretically) • Smaller residence time (smaller vessel) • Needs pressure vessel • No need for containment(e.g. dyke) • More sensitive to surge • Faster upset recovery • Water temperature might need to be increased by injecting steam (affect heat integration of the plant) • Has built –in oxygen removal system • Has internal clean and dirty backwash compartments for after filter • Does not have any internal mechanical mechanism (less prone to mechanical problems) • The temperature of water out of HLS should be decreased if it is higher than 100°C and eventually goes to BFW tank • Water out of HLS has higher temperature: more problem in downstream Ion Exchange design and operation 	<ul style="list-style-type: none"> • Operating temp between 60°C to 85°C • Bigger residence time (bigger tank) • Can be done in atmospheric tank (e.g. API 650) • Needs containment (because it is a tank) • Less sensitive to surge • Slower upset recovery • Does not have built-in oxygen removal system so oxygen removal system so oxygen scavenger injection system should be designed based on higher dissolved oxygen • Does not have internal clean and dirty backwash compartments for after filter. External tanks should be provided • Has internal mixer and rotating rake (prone to mechanical problems)

In the following section the tasks & duties of each segment of a lime softener is explained.

REACTOR

Reactions and Stoichiometry of lime softening

“Lime” in the name of “lime softening” is based on it being the main added chemical in this

process. At first sight, lime softening seems strange: removing hardness by adding lime which is a type of hardness. Unlikely as it may seem, it works! Lime (CaO) or hydrated lime (Ca(OH)₂) can be used for this purpose. Technically, we do not like the Ca portion of the lime formula; it is that hardness we want to remove. We like the

right side of formula, OH which represents a “base”.

The system removes hardness components by converting it to the low soluble salt versions of hardness ions: removing calcium by converting it to calcium carbonate (CaCO₃) and removing

magnesium by converting it to magnesium hydroxide (Mg(OH)₂).

CaCO₃ can be generated by adding sufficient CO₃²⁻, carbonate, to calcium, while Mg(OH)₂ can be generated using the sufficient amount of OH. The name of this operation is “Excess Lime Softening”.

Since removing magnesium hardness is more expensive than removing calcium hardness, in cases where magnesium concentration is low (<40 ppm) or residual tolerable hardness at downstream of lime softener is not small enough, then the lime softening process can be done by removing calcium through converting it to calcium carbonate (CaCO₃) and magnesium to magnesium carbonate (MgCO₃). Magnesium carbonate has a higher solubility than Mg(OH)₂, thus producing a water with higher residual hardness. The name of this operation is “Lime Softening”. The amount of required chemicals and generated sludge is different in lime softening operations compared to excess lime softening.

Usually Excess Lime Softening is the more attractive choice for water treaters even though it consumes more lime. Therefore, for the rest of this article we will be focusing on “excess lime softening”.

As it was mentioned converting Mg to Mg(OH)₂ can be done by adding a base to the system. The cheapest base is Lime. But hydrated lime, caustic, and even soda ash may be used for this purpose. “Caustic Softening” can be used in smaller capacity operations when the high cost of Caustic is not important and they want to avoid headaches of using Lime slurry and involved dirtiness.

Converting Ca to CaCO₃ would be easy if we had enough carbonate species in water. The good news is that Carbonate equilibrium is a big part of the equilibriums in natural waters. Therefore, the only thing that should be done is to “push” the equilibrium to produce a higher concentration of CO₃²⁻. In the HCO₃⁻ → H⁺ + CO₃²⁻ reaction, by consuming more H⁺, equilibrium “leans” to the right and generates more CO₃²⁻. And “consuming” H⁺ means adding base to the system.

This is an incredibly convenient occurrence; By adding a base to the system, we make a good environment to convert Calcium to Calcium Carbonate and at the same time, Magnesium to Magnesium Hydroxide.

If there are not enough carbonate species in the system, then they should be added through an external source. Soda Ash (Na₂CO₃) is a popular chemical to

add carbonate content of water. Even though Soda ash is a base by itself but it cannot be replaced by any other base. The reason is here we are looking for a compound which provide carbonate species’ in water.

In applications where Lime and Soda Ash both need to be added, it is claimed that instead; Caustic, NaOH, can be added. The ground for this claim is this reaction equation: Ca(OH)₂ + Na₂CO₃ → CaCO₃ + NaOH Hydrated lime and soda ash react and generate caustic. Although the logic behind this theory is correct, but this application decreases the flexibility of operation because by adding Caustic, a fixed ratio of Ca(OH)₂ and Na₂CO₃ is always applied.

When lime usage is low, hydrated lime is the first choice but in higher usages (more than 100-200 m³/hr) lime and dolomite will be more competitive choices.

To be able to predict the type and amount of required chemicals in a lime softener at the beginning, different types of hardness in water should be identified.

Hardness can be categorized as “temporary hardness” and “permanent hardness” (Table -4).

Table - 4

	<i>Calcium Hardness</i>	<i>Magnesium Hardness</i>
<i>Temporary</i>	Calcium associated with Bicarbonate	Magnesium associated with Bicarbonate
<i>Permanent</i>	Calcium associated with other Anions	Magnesium associated with other Anions

The type of hardness, if it is calcium type or magnesium type, or temporary or permanent can be determined from water analysis and using Table – 5 in mg/L as CaCO₃. In the table, whenever you are faced with a negative number, use zero instead.

Table - 5

	<i>Calcium Hardness</i>	<i>Magnesium Hardness</i>
<i>Temporary</i>	Minimum of: Ca and HCO ₃	Minimum of: Mg & (HCO ₃ -Ca)
<i>Permanent</i>	Ca-Temp. Ca	Mg- Temp. Mg

Table - 6 summarizes the main duty of each chemical in a hardness removal task. This table can be used instead of a traditional ladder diagram which was more tedious. For example the table shows that for removing temporary calcium hardness, lime is the only required chemical.

Table - 6

	<i>Calcium Hardness</i>	<i>Magnesium Hardness</i>
<i>Temporary</i>	Hydrated Lime(or Lime)	Lime(or Lime)
<i>Permanent</i>	Soda Ash	Hydrated Lime(or Lime) + Soda Ash
<i>CO₂</i>	Hydrated Lime(or Lime)	
<i>PH increase</i>	Hydrated Lime(or Lime)	

From the Table – 6 or 7 it is noticed Lime is required for all temporary harnesses. For permanent Calcium hardness only Soda ash is needed. Permanent

Magnesium hardness is the only hardness which needs addition of two chemical for removal.

The Table – 8 shows the chemical consumption per mass (weight) of different types of hardnesses in water as CaCO₃.

Table - 7

	<i>Calcium Hardness</i>	<i>Magnesium Hardness</i>
<i>Temporary</i>	Hydrated Lime: 0.74 time mass of Temporary Ca Hardness in mg of CaCO ₃	Hydrated Lime: 1.48 time mass of Temporary Mg Hardness in mg of CaCO ₃
<i>Permanent</i>	Soda Ash: 0.96 time mass of Permanent Ca Hardness in mg of CaCO ₃	Hydrated Lime: 0.74 + Soda Ash 0.96 time mass of Permanent Ca Hardness in mg of CaCO ₃
<i>CO₂</i>	Hydrated Lime: 1.7 time mass of CO ₂ in mg of CO ₂	
<i>PH Increase</i>	Consuming all residual Carbonate and Bicarbonate and required Hydrated lime to reach the target PH.	

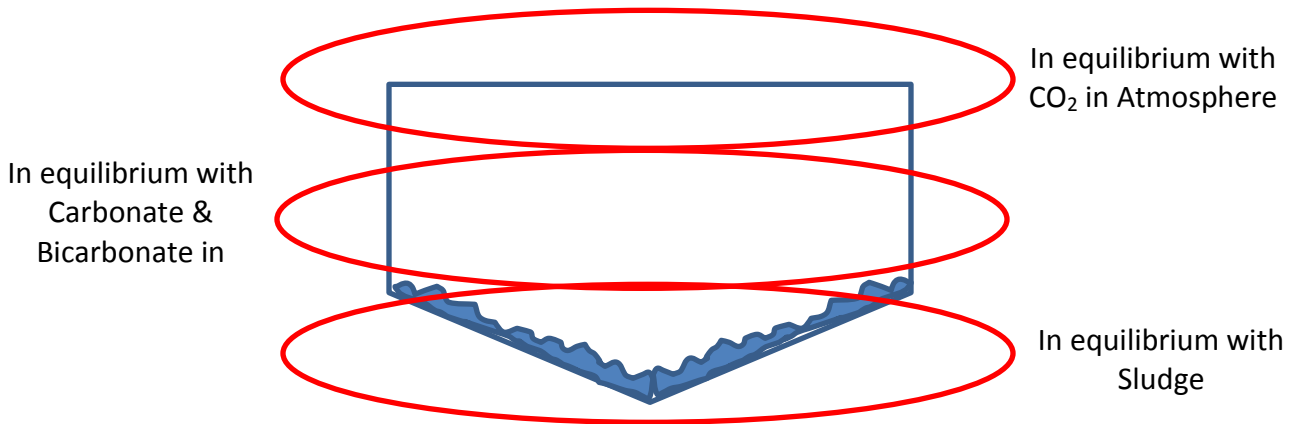
Thermodynamics of lime softening

For hardness, there could be three groups of reactions that dominate the outlet concentration of hardness ions. The first one is the equilibrium of carbonate system in open systems with air at the

surface of water in the reactor, the second one is the equilibrium of ions with precipitated calcium carbonate and magnesium hydroxide, and the last one is carbonate system equilibrium in closed systems. The action area of each equilibrium are depicted in Fig-2.

Those equilibriums basically compete with each other to define outlet hardness content. In the same conditions, the minimum hardness attained in the dominant condition of system is the second equilibrium or precipitation reactions.

Fig- 2



In the first mechanism, hardness concentration is determined by carbonate concentration in water

which is controlled by concentration of carbon dioxide (CO₂) in the air.

In the second mechanism, K_{sp} or solubility product of precipitants determine the hardness in outlet.

In a closed system without precipitation, hardness is limited to its condition as it bonds with bicarbonate ions or the third equilibrium.

One aspect of different mechanical designs of lime softeners is minimizing the action area of equilibrium group one and three and maximizing precipitation conditions in a lime softener vessel.

The optimum condition is achieved by preparing a completely mixed “pool” that precipitates particle suspends in almost every corner. This is the bases of “Solid Contact” lime softeners. In “sludge blanket” systems, the optimum condition is attained by recirculating freshly-reacted stream through a bed of already-precipitated particles.

If a lime softener can be assumed as a “equilibrium” reactor, it can be assumed that whole bulk of water inside is in equilibrium with precipitated sludge. In this hypothetical situation, the required ph to get a target, outlet hardness can be find by the Fig-3 diagram approximately.

Fig-3

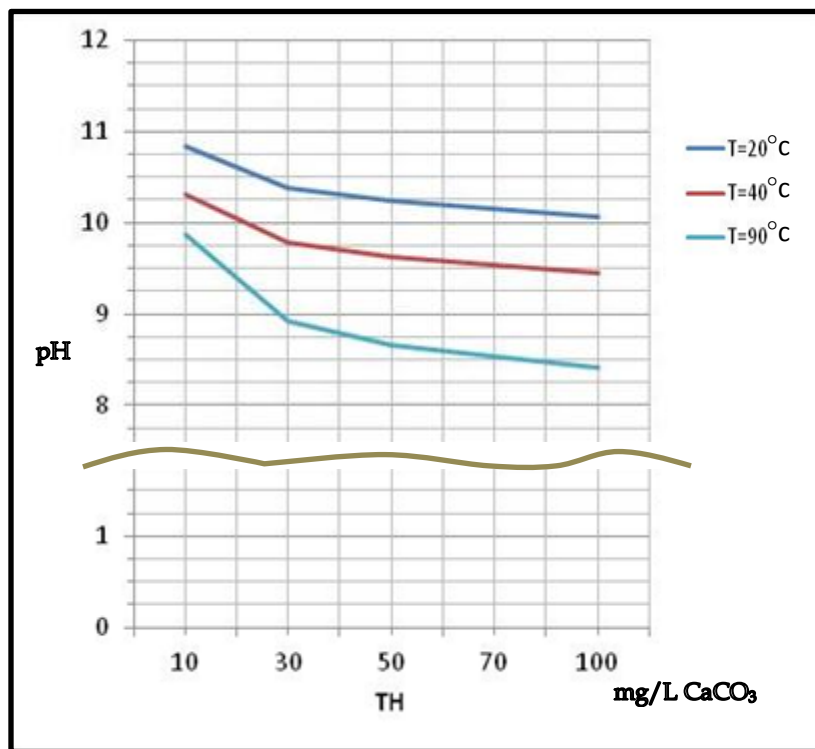


Fig-3 is developed by solving the multiple equilibriums occur in a lime softener. One limitation that Fig-3 has is that Solubility Product(Ksp) of Magnesium Hydroxide considered constant and independent of the temperature. This limitation is because temperature dependency of Ksp of Mg(OH)₂ is not available.

Kinetics of Lime Softening

The speed of a reaction depends mainly on temperature, the presence of excess reactants, keeping precipitates in contact with reactants, and eliminating or decreasing interfering ions.

Having excess OH⁻ in water (high PH) and keeping low free carbonate (CO₃⁼) will increase

crystallization rate of Mg(OH)₂ and CaCO₃ respectively.

PRECIPITATOR

The main duty of the precipitator is to provide a good environment to promote precipitation and crystallization. However, crystallization is not the main purpose. In crystallization the goal is generating crystals with a size

bigger than 200-600 micron but in a lime softener, the sludge is not a “product” so the particle size is not very important. The only aim here is to generate particles with a size larger than 100 micron-which is the preferred size for the clarification section. The particle size grows close to 100 micron by the addition coagulant and flocculant. The only feature here that is borrowed from the crystallization industry is seeding.

Two phenomena happen in two zones which are:

1. Flash Mixing Zone: In which reaction and coagulation happens
2. Slow Mixing Zone: In which flocculation happens

In conventional Coagulation-flocculation systems each of these zones need specific residence time,

and required energy for mixing. In such systems mixer is needed to provide the required energy for mixing in each zones, however in WLS’s a mixer is only needed for flocculation zone and in HLS’s there is no need to mixers at all. This is because of high temperature of water which provides enough energy. The residence time of flash mixing zones in CLS is between 0.5 to 2 minutes and for slow mixing zone between 0.5 to 0.75 hours.

Flocculant is needed to trap the smaller particles and make larger particles. Coagulants are necessary when the particles are less than 1-5 microns and surface charges/forces are strong. In some cases it may be decided to not inject coagulant when it becomes clear that particles do not carry surface charges.

In the early days, the three stages of lime softening were done in three separate basins. Later it was recognized that by recycling a portion of newly generated sludge from the precipitation basin back to the reactor, a denser sludge may be produced. After that, new designs began incorporating various combinations of the three stages. Lime softeners also can be classified based on the way the sludge is brought to contact with particles. In conventional type LS, there is no sludge recycle. When there is recycle sludge, it could be mixed with all existing sludge in a completely mixed basin or it can be left to form a layer of sludge (sludge blanket) and forced into the stream comprised of new and small particle impregnate through that sludge blanket. These three types of LS system are listed in Table-8.

Table - 8

<i>Type</i>	<i>Description</i>
<i>Conventional</i>	Without sludge recycle
<i>Solid Contact</i>	With completely mixed recycled sludge
<i>Sludge blanket</i>	With recycled sludge as impregnating blanket

These two theoretical types of recycled sludge lime softeners (solid contact or sludge blanket) are at two ends of the spectrum, it could be assumed that some

designs are closer to mixed sludge type and others are closer to sludge blanket type. Generally speaking, WLS’s work mainly based on solid contact type and HLS’s work in

sludge blanket mode (Table 9). However operation of a sludge blanket lime softener in solid contact mode is doable.

Table - 9

	<i>WLS</i>	<i>HLS</i>
<i>Solid Contact</i>	✓	
<i>Sludge blanket</i>		✓

CLARIFIER

The diameter of a softener is dictated by the clarification section. In the absence of a pilot test, the clarification section can be designed based on the falling velocity of precipitating particles. A design criterion is using a rise equal to half the rate of falling velocity. For the sake of simplicity, the Stoke's law may be used for falling velocity calculations but then the challenge

is estimating particle size and density.

De-Sludging

The sludge composition is dictated by water analysis and chemicals which are added to the system. Water content of sludge may range be from 5% wt to 30% wt, based on the design of the lime softening system and type of operation.

Sludge is mainly composed of calcium carbonate (CaCO_3),

magnesium hydroxide ($\text{Mg}(\text{OH})_2$), adsorbed silica on magnesium hydroxide ($\text{Mg}(\text{OH})_2 \cdot \text{SiO}_2$), non-reacted lime ($\text{Ca}(\text{OH})_2$), non-reacted magox (MgO_2), slaked magox ($\text{Mg}(\text{OH})_2$), adsorbed organics on sludge, and oil droplets trapped in precipitates, if any.

Table 10 summarizes the different component in the sludge in an excess lime operation.

Table- 10

	<i>Calcium Hardness</i>	<i>Magnesium Hardness</i>
<i>Temporary</i>	CaCO_3 : 2 time mass of Temporary Ca Hardness in mg of CaCO_3	CaCO_3 : 2 time + $\text{Mg}(\text{OH})_2$: 0.58 time mass of Temporary Ca Hardness in mg of CaCO_3
<i>Permanent</i>	CaCO_3 : 1 time mass of Temporary Ca Hardness in mg of CaCO_3	CaCO_3 : 1 time + $\text{Mg}(\text{OH})_2$: 0.58 time mass of Temporary Ca Hardness in mg of CaCO_3

The consistency of sludge is determined not only by its water content, but also by its

composition of solids. High percentage of magnesium hydroxide—which is a gelatinous

solid—makes the sludge lighter and hard to dewater but less abrasive. Water with a high

calcium content leads to a sludge which is easy to dewater but more abrasive.

Desludging from the bottom of the lime softening basin is usually intermittent. This intermittent operation is not due to designer or operator preference but rather a result of the low flowrate of sludge in most lime softening operations. This flowrate causes the sludge to settle as it passes through small bore pipes (2" if it supposed to go over the pipe rack). The other reason for intermittent desludging is the prevention of wasting water along with a too-dilute sludge. Generally the de-sludging duration is the time it takes to empty the sludge pit which happens after each lap of the rake(if sludge collection is by rake rotation)or time for sludge to "slide" the bottom cone(if sludge collection is by the high slope of bottom of the lime softener). The sludge can be just landfilled or sent to further units for dewatering.

Other Tasks for Lime Softener

The precipitation that results in lime softeners can be taken advantage of. All other types of precipitation removal methods, which are a group of removal methods for dissolved water contaminants, can be done in lime softeners too. In this respect, the original lime precipitates synergize the other precipitations through the phenomenon of co-precipitation.

Lime softeners can also remove Silica, organics (TOC) and oil globules in small concentrations

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and even work as a partial disinfection basin.

Magnesium oxide (Magox) is used for silica removal, the mechanism of which utilizes adsorption and possibly partial reaction. Silica will co-precipitate with magnesium oxide/hydroxide in high pH environment, and may be observed as magnesium silicate in co-precipitated sludge.

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Toghraei has over 20 years' experience in the field of industrial water treatment. His main expertise is in the treatment of wastewater from oil and petrochemical complexes. For the past nine years he has taken on different technical and leadership roles in water treatment areas of SAGD projects. Toghraei has received a B.Sc. in chemical engineering from Isfahan University of Technology and an M.Sc. in environmental engineering from the University of Tehran, and is a member of APEGA.