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Viability of using chemical speciation software in the study of the removal of Ca^{2+} and Mg^{2+} in industrial waters

Viabilitat de la utilització d'un software d'especiació química en l'estudi de l'eliminació de Ca^{2+} i Mg^{2+} en aigües industrials

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Satisfaction lies in the effort, not in the attainment. Full effort is full victory.

Mahatma Gandhi

REPORT

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1. SUMMARY

In this project the prediction of the removal of dissolved calcium and magnesium from the industrial waters that they feed some processes such reverse osmosis (RO) system, boilers, coolers or heat exchangers has been study. The removal or hardness is necessary to avoid scaling problems in the equipment or in the pipes. The scaling may reduce the efficiency of the processes increasing costs and energy consumption.

The main objective of the project is to study the viability of a chemical speciation software, OLI Analyzer Studio®. The software is used to predict the reduction of dissolved calcium and magnesium.

The removal method used in the simulations is the lime and soda ash softening (among others, chemical precipitation is one of the most used methods for water softening). Different simulations have been done with OLI based in different water characteristics obtained from two sources: scientific articles and laboratory Jar Tests.

From the waters composition extracted from scientific articles, some simulations are realized to obtain water with minimum content in calcium and magnesium (under 5 ppm). These results are compared with the results obtained from stoichiometric calculations. Furthermore, if the removal values of the article are available, these are compared with the results obtained from OLI.

From the waters composition extracted from the laboratory Jar Tests, some simulations are realized with the same chemical doses to see if the remaining amounts are similar.

The obtained values show that OLI is an effective estimation software that allows to predict the consumptions of the products necessary in the chemical precipitation. It is very important to dispose of a well-defined water composition. OLI is a tool that allows us to save time and costs in the laboratory.

2. RESUM

El projecte es basa en la predicció de l'eliminació del calci i del magnesi dissolt en aigües industrials les quals alimenten certs processos com poden ser un sistema d'osmosi inversa, una caldera, un refrigerador o un bescanviador de calor. Aquesta eliminació és necessària per evitar problemes d'incrustacions en els equips o les canonades. Aquestes incrustacions poden reduir l'eficiència del procés, incrementar els costos i el consum energètic.

L'objectiu principal del projecte és estudiar la viabilitat d'un software d'especiació química, OLI Analyzer Studio®. El software és utilitzat per predir la reducció del calci i del magnesi dissolt.

El mètode d'eliminació utilitzat en les simulacions és l'estovament (mitjançant precipitació química que és un dels mètodes més utilitzats per eliminar duresa a l'aigua) amb l'hidròxid de calci i el carbonat de sodi. Es realitzen diferents simulacions amb OLI basades en diferents aigües obtingudes de dues fonts: articles científics i proves realitzades al laboratori.

A partir de les composicions d'aigües extretes d'articles científics, es realitzen simulacions per obtenir aigua amb un mínim de calci i magnesi (per sota de 5 ppm), aquests resultats es comparen amb els resultats obtinguts per càlculs estequiomètrics. A més, si es disposa de valors d'eliminació a l'article, aquests són comparats amb els obtinguts amb OLI.

A partir de les composicions d'aigües extretes de proves realitzades al laboratori, es realitzen simulacions amb les mateixes dosis dels productes per veure si les quantitats restants són similars.

Els valors obtinguts mostren que OLI és un software de predicció molt eficaç que ens permet predir el consum dels reactius utilitzats en la precipitació química. És molt important disposar d'una composició de l'aigua molt ben definida. OLI és una eina que ens permet estalviar temps i costos al laboratori.

3. INTRODUCTION

3.1. WATER HARDNESS

Hardness is an important water quality parameter determining the suitability of water for domestic and industrial uses. Hardness is the term often used to characterize a water that requires considerable amounts of soap to produce foam. Hard water causes scaling on membranes, pipes, and hot boilers. Also causes valves to stick due to the formation of calcium carbonate deposits and leave stains in plumbing fittings [1, 2].

Hard water contains high levels of different types of polyvalent ions, mainly magnesium and calcium. Hardness is defined as the sum of the calcium and magnesium cation concentrations. Other types of cations can contribute to this hardness, such a strontium, iron, aluminum or manganese, although to a lesser degree. The natural waters travel through rocks and soil picking up minerals including calcium and magnesium. The hardness of the water is usually expressed in ppm (mg/L) of calcium carbonate ($CaCO_3$) or meq/L [2, 3].

Two different kind of hardness can be considered [3, 4]:

- *Temporary hardness* or *carbonate hardness* is a type of water hardness caused by the presence of dissolved bicarbonate minerals ($Ca(HCO_3)_2$ and $Mg(HCO_3)_2$) and it can be reduced either by boiling the water, or by the addition of calcium hydroxide (named lime, $Ca(OH)_2$) by the process called lime softening. Boiling and high pH promote the formation of carbonate from the bicarbonate and precipitates calcium carbonate. This hardness is chemically equivalent to the alkalinity where most of the alkalinity in natural waters is caused by the bicarbonate and carbonate ions.
- *Permanent hardness* or *non-carbonate hardness* is the hardness that cannot be removed by boiling. It’s usually caused by calcium and magnesium compounds of sulfate, chloride, nitrate that are dissolved in water, which don’t precipitate as the temperature increases. To remove the permanent hardness some additional processes may be necessary.

Total Hardness (TH) = Carbonate Hardness (CH) + Non-Carbonate Hardness (NCH)

A classification into hard and soft water can be used (Table 3.1). However, a single number does not adequately describe hardness because is the complexity of the mixture of minerals dissolved in the water, together with the water pH and temperature that determine the behavior of the hardness.

Classification	Hardness [ppm $CaCO_3$]
Soft	0-75
Moderately Hard	75-100
Hard	100-300
Very Hard	> 300

Table 3.1 Hardness Classification [4]

The hardness type (carbonate or non-carbonate) can be analyzed using a bar diagram (Figure 3.1). The bar diagram shows the relative proportions of the most important chemical species in the water. Cations are placed above the anions on the diagram. The sum of the cation and anion charge should be equal to zero to keep electroneutrality, otherwise there is an error in analysis or computations. Units used to express hardness are mg/L $CaCO_3$ or meq/L [4, 5]. Below an example [4] of utilization of the bar diagram is displayed. Table 1.2 includes the values from a water analysis further plotted in Figure 3.1 Table 3.2 also shows the concentrations in the proper units (meq/L and mg/L as $CaCO_3$).The ions given in Table 3.2 are the most significant in the water.

Chemical specie	Concentration [mg/L] (1)	Equivalent Weight (2)	Concentration [meq/L] (3) = (1) / (2)	Concentration [mg/L $CaCO_3$] (4) = (3) * 50
Ca^{2+}	75.0	20.0	3.7	187.0
Mg^{2+}	40.0	12.2	3.3	164.0
Na^{+}	10.0	23.0	0.4	22.0
HCO_3^{-}	300.0	61.0	4.9	246.0
Cl^{-}	10.0	35.5	0.3	14.0
SO_4^{2-}	109.0	48.0	2.2	113.0

Table 3.2 Example of ion concentration from a water analysis [4]

Now, the bar diagram can be built [Figure 3.1]

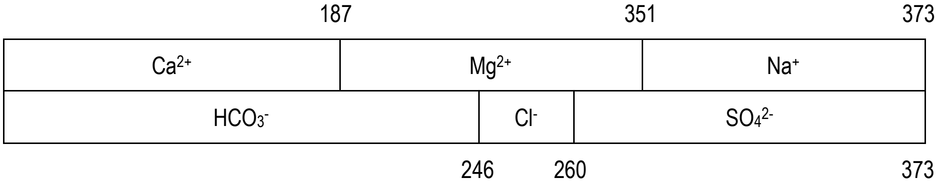


Figure 3.1 Bar diagram of raw water in mg/L as $CaCO_3$ (Self production from [4])

Analayzing Figure 3.1 the water content is the following:

- Total Hardness (T.H.) = $[Ca^{2+}] + [Mg^{2+}] = 187 + 164 = 351$ mg/L $CaCO_3$
- Alkalinity = Bicarbonate Alkalinity = 246 mg/L $CaCO_3$
- Carbonate Hardness (C.H.) = Alkalinity = 246 mg/L $CaCO_3$
- Non-Carbonate Hardness (N.C.H.) = T.H. – C.H. = 351 – 246 = 105 mg/L $CaCO_3$

The hardness is the main cause of scaling in membranes, pipe lines, boilers, heat exchange equipment, etc. Scaling is composed mainly by calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$) and calcium sulfate ($CaSO_4$). The precipitation is caused by thermal decomposition of bicarbonate ions but also happens to some extent when the solubility product of some salt is exceed. The scaling reduces the efficency of the processes, increases costs and energy consumption [4].

An special case is under investigation: water as a feed to reverse osmosis process (RO) with a semi-permeable membrane. The reverse osmosis (RO) is often used to treat saltwater or brackish water to create potable water. It's also used in a several of industrial processes to produce water with a high level of purity. A stream of water, called the feed water, enters the RO system and is pressurized against a semi-permeable membrane, and it produces two streams, the permeate and the concentrate. The permeate is dionized, purified water, and the concentrate is the rejected water containing a high level of dissolved ions. The concentrate is sent to drain or a portion of it is recycled back to the feed stream to increase the system's overall water recovery. The problem is that the calcium and magnesium compounds of the hard feed water, precipitate onto the membrane reducing the production surface. Scaling usually is very difficult to remove and the membrane requires a good maintenance, chemical products, and cleaning which may eventually damage the membrane.

3.2. SOFT WATER APPLICATIONS

Due to high levels of calcium and magnesium, many types of equipment fail to work properly, which can lead to an increase in energy costs and complete failure of the equipment. Many plants use the soften processes listed above. These processes such as reverse osmosis (RO), boilers or coolers will be introduced below.

3.2.1. REVERSE OSMOSIS (RO) SYSTEMS

Reverse osmosis (RO) systems usually have a softening pretreatment to reduce the hardness of the water which will be treated. Reverse osmosis (RO) is a membrane-based demineralization technique used to separate dissolved solids, such as ions, from solution (most applications involve water-based solutions, which is the focus of this work). Membranes in general act as perm-selective barriers that allow some species (such as water) to selectively permeate through them while selectively retaining other dissolved species (such as ions). This process requires a pressure greater than the osmotic pressure. This pressure forces water to pass through the membrane. Water now moves from the compartment with the high-concentration solution to that with the low concentration solution. Thus, relatively pure water passes through membrane while dissolved molecules or ions are retained [6].

Most reverse osmosis systems fall into three main categories [7]:

- Traditional reverse osmosis systems operate with a feed of 200 psi to 400 psi. This means that a moderate amount of energy is used to pump the feed water through the membranes to overcome the osmotic pressure.
- Brackish reverse osmosis systems tend to operate at over 400 psi and require more energy is necessary. Brackish water has higher osmotic pressure than water that is fed through a traditional reverse osmosis system.
- Desalination reverse osmosis systems operate at 800 psi to 1200 psi. At 800 psi and above, a special high pressure pump is required. These pumps produce high pressure feeds and are built of special alloys. Because of the great amount of energy required to overcome the osmotic pressure, energy recovery devices are typically used.

There are many applications of reverse osmosis process especially due to water scarcity. Common uses include drinking water, humidification, ice-making-biomedical applications, laboratory applications, pharmaceutical production, kidney dialysis, water used in chemical processes, cosmetics, hemodialysis, etc. [8].

Soften the water that is involved in a reverse osmosis process is necessary to avoid operational problems. When the hard water is fed to the membrane produces scaling. This scaling is caused by the precipitation of different calcium and magnesium compounds on the surface of the membrane.

In addition to a pretreatment based in softening processes, in many reverse osmosis processes antiscalants are added. This addition is done in the feed stream of the membrane. An antiscalant is a chemical that interferes with precipitation reactions in three primary ways [8]:

- *Crystal modification*: It is the property of an antiscalant to retard the nucleation process.
- *Dispersion*: It is the ability of an antiscalant to stop the growth of the crystals.
- *Threshold inhibition*: It is the ability of an antiscalant to keep supersaturated solutions of sparingly soluble salts. This antiscalant multiplies the solubility product of the compound. If there is a good antiscalant it multiplies for five or for four the solubility product of the compound. If there is a normal antiscalant it multiplies for three or for two the solubility product.

3.2.2. BOILERS

The water pretreatment has a special importance in the efficiency, in the life and in the security in the operations of industrial boilers. This pretreatment is fundamental for the boiler to have a long life without operational problems. With this pretreatment, corrosion problems and scaling problems will be decreased [9, 10].

The scaling in boilers causes a serious problem due to their low conductivity. This low conductivity acts as a thermal insulating and causes many refrigeration problems in the metallic surfaces. It may even cause many overheating problems [10].

Calcium and magnesium are inversely soluble to temperature. As the temperature rises (such as in a boiler process), their solubility decreases, eventually causing the calcium and magnesium compounds to precipitate. They precipitate first on the heat transfer surfaces (i.e., boiler tubes) because these surfaces have the highest temperature. In addition, the precipitation problem is compounded by the saturation of the calcium and magnesium. As the boiler water evaporates, it leaves these ions behind, increasing their concentration. Over time, the minerals will saturate and precipitate as scale. The speed at which saturation is reached also depends on the rate of condensate return. The less condensate is returned, the more water is made-up. The more minerals are introduced, the faster the saturation point will be reached. Low calcium and magnesium in water becomes even more crucial in low condensate return applications, such as humidification, or other direct steam injections. Furthermore, the scaling will insulate the heat transfer surfaces, decreasing the heat transfer efficiency, and increasing energy cost. Finally, the boiler is subjected to a higher stack temperature, due to poor heat recovery. The heat transfer surfaces are also subjected to higher temperature, due to poor heat transfer. Both increase thermal loading which add more stress on the boiler, eventually reducing its life expectancy [11].

The feed water for a boiler must be free from calcium and magnesium to ensure efficiency. Otherwise, they will increase production costs and decrease product quality. The lower the hardness level, the better the water quality for a steam boiler process [11].

3.2.3. COOLERS

Cooling towers are another common application for industrial softened water. Cooling towers can operate much more efficiently with softened water. This can help to realize a drastic reduction in maintenance, chemical feed quantity, and the volume of water required for operation [7].

The evaporative cooler uses a piping system to carry water to the heat transfer section. Hard water will build up scaling, which can reduce or completely cut off water flow. Also soft water can build up scaling, but with hard water, this process is faster. At the point of evaporation, residue will build up as water vapor escapes and the dissolved minerals are left behind on the surface of the evaporator. This mineral residue will act as an insulator, reducing the cooling effect gained by the evaporator. Depending upon the minerals left as the residue, the residue might have a corrosive effect on the evaporating surface and nearby metal fittings.

The use of hard water in this process means an evaporative cooler will need more regular maintenance to remove the residue and more frequent replacement of damaged fittings and piping. The efficiency of the cooler will drop off faster, particularly if it isn't cleaned thoroughly and often, resulting in less cooling, higher operating costs or both.

3.2.4. HUMIDIFIER

Humidification is the process of transforming water into vapor, and so it is not surprising that water type has a great impact on humidifier performance, maintenance requirements, humidification vapor quality, and efficiency of operation [8].

Soft water provides for easier maintenance of a humidifier. When hard water is evaporated, the mineral residue consists of a hard scale which normally requires some drastic treatment (such as chipping or acid) for its removal. When soft water is used, the residue is commonly called soft and usually be removed by flushing the unit with water or going over the surface with a brush. Hard water presents a problem for all humidifiers, and filters have to be changed more often. The use of hard water requires more frequent cleaning [12].

3.2.5. HEAT EXCHANGERS

Hard water causes heat exchanger scale. It has a drastic effect on the efficiency and lifespan of heat exchanger. The scaling that it forms is a very poor conductor of heat and any heat transfer surface on which scaling is laid down will experience a reduction in efficiency. The result of this is that more fuel will be required to raise the temperature of the water to the required level because the heating time required will be increased. Studies have shown that a 25 mm thick layer of scaling on a heat exchange surface will reduce heat transfer by 95% [13], and this has implications for energy costs. Just a 1 mm layer of scaling may increase energy costs by 7,5% [13], while a 12 mm layer will raise this increase to 70% [13]. Increased use of fuel also increases CO_2 emissions. As well as losses in efficiency, pipes and components can become partially or completely blocked leading to circulation and flow issues.

4. OBJECTIVES

The project aims to study the removal of calcium and magnesium from industrial process waters. This objective is especially focused in the study of chemical precipitation among the other available technologies.

The feasibility and suitability of the chemical precipitation was studied through simulation tools. To accomplish the objective, OLI Studio Analyzer®, chemical speciation software, was used to predict the reduction of water hardness (removal of dissolved calcium and magnesium).

Different simulations and comparisons were done to verify the usability of this chemical speciation software in the prediction of chemicals consumptions. This would help engineers in two ways: allowing an approach to the size of the treatment (initial step in the design of chemical treatment plants, even before to lab tests) and predicting changes in already operating physic-chemical treatments due to changes in the composition of the feed water.

5. REMOVAL OF CALCIUM AND MAGNESIUM

As stated above, the removal of calcium and magnesium from hard water is very important to avoid all the problems that can cause scaling. There are four principal methods of softening hard water.

- Chemical precipitation: lime and soda ash are added to precipitate hardness compounds which are then removed by clarification and filtration.
- Ion exchange: the nature of the compounds is changed by passing the water through a bed of ion-exchange resin.
- Membrane processes: nanofiltration removes bivalent or trivalent ions at an efficiency of about 80-85% and monovalent ions at an efficiency of up to 40%.
- Electrodialysis: this is an electrochemical separation process in which ions are transferred through ion exchange membranes by means of a direct current voltage.

The differences in the four methods are important. The selection of the softening method depends on many factors. Regardless of which water treatment is considered, the first should be tested to characterize which contaminants are present.

First experiments with the objective to achieve soft water had been performed in 1756 by Dr. Francis Home, in Edinburgh, Scotland. He was the first scientist who found out the lime capacity to soften water. The first plant to soften water was built in Plumstead, England, in 1854. It was used the process of Thomas Clark, a chemical university teacher. Clark patented his process in 1841. This process is a lime treatment followed by sedimentation and filtration. This plant and other that were building in 1861, 1868, and 1870 treat well water. These plants didn't use filters and didn't remove non-carbonate hardness. In 1856, Dr. Porter in London suggested the soda ash use to remove non-carbonate hardness. In 1878, Ashby got a patent to remove non-carbonate hardness with soda ash or potassium carbonate. England had more than 50 soften plants in 1900. The first soften plant in the USA was building in Oberlin, Ohio, in 1903 [14].

In last years, new processes have been developed, and nowadays the four softening methods listed above are the most important industrial methods.

The processes will be described with more details in the following sections.

5.1. CHEMICAL PRECIPITATION

Chemical precipitation is an effective treatment process for the removal of many contaminants and it's used to reduce raw water hardness, alkalinity, silica, and other constituents [4]. The removal of substances from water by precipitation depends primarily on the solubility of the various complexes formed in water. For example, heavy metals in water will form both hydroxide and carbonate solids forms. These solids have low solubility limits in water. Thus, as a result of the formation of insoluble hydroxides and carbonates, the metals will be precipitated out of solution [4, 15, 16].

The discussion of the application of chemical precipitation in water treatment presented in this project will emphasize the reduction in the concentration of calcium and magnesium (water softening).

A chemical reaction is said to have reached equilibrium when the rate of the forward reaction is equal to the rate of the reverse reaction so that no further net chemical change occurs. A general chemical reaction that has reached equilibrium is commonly expressed as [4]:

$$\boldsymbol{aA + bB \rightleftharpoons cC + dD} \qquad \textbf{(5.1)}$$

The equilibrium constant K_{eq} for this reaction is defined as:

$$\boldsymbol{K_{eq} = \frac{(C)^c(D)^d}{(A)^a(B)^b}} \qquad \textbf{(5.2)}$$

Where the equilibrium activities of the chemical species A, B, C and D are denoted by (A), (B), (C) and (D) and the stoichiometric coefficients are represented as a, b, c, and d. By convention, the activities of solid material, such as precipitates, and solvents, such as water, are taken as unity.

The state of solubility equilibrium is a special case that may be attained either by formation of a precipitate from the solution phase or from partial dissolution of a solid phase. The precipitation process is observed when the concentrations of ions of a poorly soluble compound are increased beyond a certain value. When this occurs, a solid that may settle is formed. Such a process may be described by the reaction:

$$\boldsymbol{A^+ + B^- \rightleftharpoons AB_{(s)}} \qquad \textbf{(5.3)}$$

Where (s) denotes the solid form.

Precipitation formation is both a physical and chemical process. The physical part of the process is composed in two phases: nucleation and crystal growth [16].

Nucleation begins with a supersaturated solution, a solution that contains a greater concentration of dissolved ions than can exist under the equilibrium conditions. Under such conditions, a condensation of ions will occur, forming very small particles. The process can be enhanced by the presence of performed nuclei that are introduced.

Crystal growth follows nucleation as ions diffuse from the surrounding solution to the surfaces of the solid particles. This process continues until the condition of supersaturation has been relieved and equilibrium is established. When equilibrium is achieved, a saturated solution will have been formed, a solution in which undissolved solute is in equilibrium with solution.

No compound is totally insoluble. Consider the following dissolution reaction occurring in an aqueous suspension of the sparingly soluble salt:

$$\boldsymbol{AB_{(s)} \rightleftharpoons AB} \qquad \textbf{(5.4)}$$

The aqueous, undissociated molecule that is formed then dissociates to give a cation and anion:

$$\boldsymbol{AB \rightleftharpoons A^{+} + B^{-}} \qquad \textbf{(5.5)}$$

The two previous equilibrium constant expressions may be manipulated to give:

$$\boldsymbol{K_{ap} = (A^{+})(B^{-})} \qquad \textbf{(5.6)}$$

Where the product of the activities of the two ionic species is defined as the thermodynamic activity product (K_{ap}). The concentration of a chemical species, not activity, is of interest in water treatment. Because dilute solutions are typically encountered, this parameter may be employed without introducing significant error into calculations.

$$\boldsymbol{K_{sp} = [A^{+}][B^{-}]} \qquad \textbf{(5.7)}$$

This is the classical solubility product expression for the dissolution of a slightly soluble compound where the brackets denote molar concentration. The equilibrium constant is called *the solubility product constant* [4]. The more general form of the solubility product expression is derived from the dissolution reaction:

$$\boldsymbol{A_{x}B_{y(s)} \rightleftharpoons xA^{y+} + yB^{x-}} \qquad \textbf{(5.8)}$$

And has the form:

$$K_{sp} = [A^{y+}]^{x}[B^{x-}]^{y} \qquad \textbf{(5.9)}$$

The value of the solubility product constant gives some indication of the solubility of a particular compound. For example, a compound that is highly insoluble will have a very small solubility product constant. Previous equation applies to the equilibrium condition between ion and solid. If the actual concentrations of the ions in solutions are such that the ion product is less than the K_{sp} value, no precipitation will occur. Furthermore, if the actual concentrations of ions in solution are so great that the ion product is greater than the K_{sp} value, precipitation will occur (assuming nucleation occurs).

If an ion of a sparingly soluble salt is present in solution in a defined concentration, it can be precipitated by the other ion common to the salt, if the concentration of the second ion is increased to the point that the ion product exceeds the value of the solubility product constant. Such an influence is called the *common-ion effect* [4]. Furthermore, precipitating two different compounds is possible if two different ions share a common third ion and the concentration of the third ion is increased so that the solubility product constants for both sparingly soluble salts are exceeded. This type of precipitation is normally possible only when the K_{sp} values of the two compounds don’t differ significantly.

The common-ion effect is an example of LeChâtelier’s principle [16], which states that if stress is applied to a system in equilibrium, the system will act to relieve the stress and restore equilibrium, but under a new set of equilibrium conditions.

Take into account that in this case it would like to remove some metals by chemical precipitation such as calcium or magnesium, the following equilibrium reaction involve metal solubility:

$$MA_{x(s)} = M^{x+} + xA^{-} \qquad \textbf{(5.10)}$$

$$K_{sp} = [Me^{x+}][A^{-}]^{x} \qquad \textbf{(5.11)}$$

The solubility product expression indicates that equilibrium concentration (in precipitation processes this is referred to as the residual concentration) of the metal in solution is solely dependent upon the concentration of A^{-}. When A^{-} is the hydroxide ion the residual metal concentration is a function of pH such that:

$$log[M^{x+}] = logK_{sp} - xlogK_{w} - XpH \qquad \textbf{(5.12)}$$

The solubility of most metal hydroxides is not accurately described by previous equation, however, because they exist in solution as a series of complexes formed with hydroxide and other ions. Each complex is in equilibrium with the solid phase and their sum gives the total residual metal concentration. For the case of only hydroxide species and a divalent metal, the total residual metal concentration is given by:

$$\boldsymbol{M_{T1} = M^{2+} + M(OH)^{+} + M(OH)_2^0 + M(OH)_3^- + \cdots} \qquad \textbf{(5.13)}$$

Due to this situation, the total residual metal concentration is a complex function of the pH. In Figure 5.1, line B shows that the lowest residual concentration will increase when the pH is either lowered or raised from this optimum value. The theoretical solubility of hypothetical metal hydroxide can be seen, where K_{sp}=10^{-10}, K_w=10^{-14} and X=2 (assumed values). In line A without complex formation and in line B with complex formation.

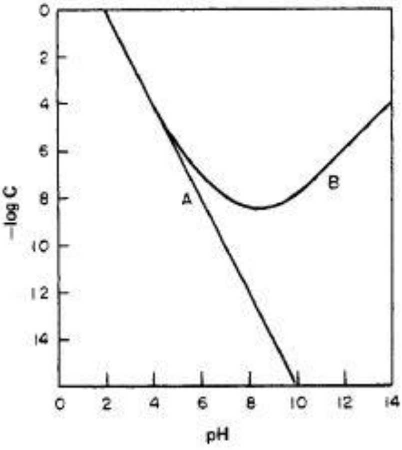


Figure 5.1 Theoretical solubility of hypothetical metal hydroxide [Benefield L.D. et al.WQAT ref.4]

Numeric estimations on metal removal by precipitation as metal hydroxide should always be treated carefully because oversimplification of theoretical solubility data can lead to error of several orders of magnitude. Many possible reasons exist for such discrepancies. For example, changes in the ionic strength of a water can result insignificant differences between calculated and observed residual metal concentrations when molar concentrations rather than activities are used in the computations (high ionic strength will result in a higher than predicted solubility). The presence of organic and inorganic species other than hydroxide, which are capable of forming soluble species with metal ions, will increase the total residual metal concentration. Two inorganic complexing agents that result in very high residual metal concentrations are cyanide and ammonia. Small amounts of carbonate will significantly change the solubility chemistry of some metal hydroxide precipitation systems. As a result, deviations between theory and practice should be expected because precipitating metal hydroxides in practice is virtually impossible without at least some carbonate present [4].

Temperature variations can explain deviations between calculated and observed values if actual process temperatures are significantly different from the value at which the equilibrium constant was evaluated. Kinetics may also be an important consideration because under process conditions the reaction between the soluble and solid species may be too slow to allow equilibrium to become established within the hydraulic retention time provided. Furthermore, many solids may initially precipitate in an amorphous form but convert to a more insoluble and more stable crystalline structure after some time period has passed.

Formation of precipitates other than the hydroxide may result in a total residual metal concentration lower than the calculated value. For example, the solubility of cadmium carbonate is approximately two orders of magnitude less than that of the hydroxide.

In conclusion, the solubility behavior of most slightly soluble salts is very complex because of competing acid-base equilibrium, complex ion formation, and hydrolysis. Still, many precipitation processes in water treatment can be adequately described when these reactions are ignored.

<u>The carbonic acid system</u>

The pH of most types of waters is generally assumed to be controlled by the carbonic acid system. The applicable equilibrium reactions are:

$$\boldsymbol{CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-} \qquad \textbf{(5.14)}$$

$$\boldsymbol{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}} \qquad \textbf{(5.15)}$$

Because only a small fraction of the total CO_2 dissolved in water is hydrolyzed to H_2CO_3, summing the concentrations of dissolved CO_2 and H_2CO_3 to define a new concentration term, $H_2CO_3^*$, is convenient. Equilibrium constant expressions for the previous equilibriums have the form:

$$\boldsymbol{K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}} \quad \textbf{(5.16)}$$

$$\boldsymbol{K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}} \quad \textbf{(5.17)}$$

Where K_1 and K_2 represent the equilibrium constants for the first and second dissociation of carbonic acid, respectively.

The total carbonic species concentration in solution is usually represented by C_T and defined in terms of a mass balance expression.

$$\boldsymbol{C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]} \quad \textbf{(5.18)}$$

The distribution of the various carbonic species can be established in terms of the total carbonic species concentration by defining a set of ionization fractions, α, where:

$$\boldsymbol{\alpha_0 = \frac{[H_2CO_3^*]}{C_T}} \quad \textbf{(5.19)}$$

$$\boldsymbol{\alpha_1 = \frac{[HCO_3^-]}{C_T}} \quad \textbf{(5.20)}$$

$$\boldsymbol{\alpha_2 = \frac{[CO_3^{2-}]}{C_T}} \quad \textbf{(5.21)}$$

Through a series of algebraic manipulations:

$$\boldsymbol{\alpha_0 = \frac{1}{1+K_1/[H^+]+(K_1K_2)/[H^+]^2}} \quad \textbf{(5.22)}$$

$$\boldsymbol{\alpha_1 = \frac{1}{[H^+]/K_1+1+K_2/[H^+]}} \quad \textbf{(5.23)}$$

$$\boldsymbol{\alpha_2 = \frac{1}{[H^+]^2/(K_1K_2)+[H^+]/K_2+1}} \quad \textbf{(5.24)}$$

The effect of pH on the species distribution for the carbonic acid system is shown in Figure 5.2. Because the pH of most waters that it will be treated is in the neutral range, the alkalinity (assuming that alkalinity results mainly from the carbonic acid system) is in the form of bicarbonate alkalinity.

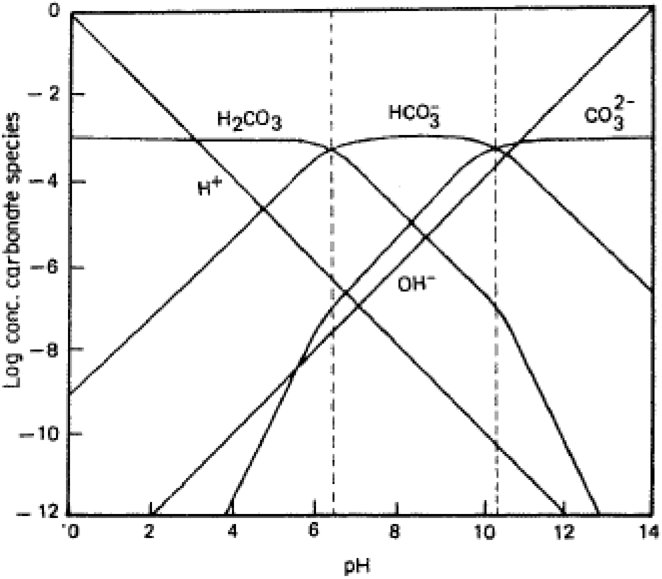


Figure 5.2 Concentration Distribution diagram for carbonic acid [Benefield L.D. et al.WQAT ref.4]

5.1.1. LIME-SODA ASH SOFTENING

Lime softening is an operation which has been used for the past 150 years to remove hardness and soften the water. Chemicals used are lime (calcium hydroxide, $Ca(OH)_2$) and soda ash (sodium carbonate, Na_2CO_3) to remove hardness either completely or partially. Caustic soda (sodium hydroxide, NaOH), can also be used instead of lime, but softening by lime and lime soda ash is generally less expensive than caustic soda softening. Lime is used to remove chemicals that cause carbonate hardness and soda ash is used to remove chemicals that cause non-carbonate hardness. Calcium carbonate and magnesium hydroxide are the less soluble calcium and magnesium compounds [4, 17, 18, 19, 20, 21].

To remove calcium and magnesium lime and soda ash are added to water. Raising the pH in the presence of alkalinity converts bicarbonates into carbonates and removes magnesium and calcium as magnesium hydroxide ($Mg(OH)_2$) and calcium carbonate ($CaCO_3$) respectively. This process turns soluble calcium and magnesium to insoluble calcium carbonate and magnesium hydroxide. The concentration of various carbonic species and the system pH play important roles in the precipitation of these two solids. These precipitates are then removed from the water by conventional processes of coagulation/flocculation, sedimentation, and filtration.

The explanation of solubility products in the previous section is applied for lime and soda softening process. In this case the calcium and magnesium will be removed as calcium carbonate and magnesium hydroxide.

The solubility equilibrium for $CaCO_3$ is described by:

$$\boldsymbol{CaCO_{3(s)} \rightleftharpoons Ca^{2+} + CO_3^{2-}} \qquad \textbf{(5.25)}$$

The addition of $Ca(OH)_2$ to a water increases the hydroxyl ion concentration and elevates the pH and as can be observed in Figure 5.2, that shifts the equilibrium of the carbonic acid system in favor of the carbonate ion. Increasing the concentration of the carbonate ion, according to LeChâtelier’s principle, shifts the equilibrium described by equation (5.25) to the left (common-ion effect). Such a response results in the precipitation of $CaCO_{3(s)}$ and a corresponding decrease in the soluble calcium concentration.

The solubility equilibrium for $Mg(OH)_2$ is described by:

$$\boldsymbol{Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^-} \qquad \textbf{(5.26)}$$

Here again, according to LeChâtelier's principle, the addition of hydroxyl ions shifts the equilibrium described by equation (5.26) to the left (common-ion effect), resulting in the precipitation of Mg(OH)2 and a corresponding decrease in the soluble magnesium concentration.

The solubility product expressions for these two equations have the forms:

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \qquad (5.27)$$

$$K_{sp} = [Mg^{2+}][OH^-] \qquad (5.28)$$

The complex ion formation reactions that contribute to the total soluble calcium concentration are:

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+ \quad (5.39) \qquad K_3 = [CaOH^+]/[Ca^{2+}][OH^-] \quad (5.30)$$

$$Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^+ \quad (5.31) \qquad K_4 = [CaHCO_3^+]/[Ca^{2+}][HCO_3^-] \quad (5.32)$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 \quad (5.33) \qquad K_5 = [CaCO_3]/[Ca^{2+}][CO_3^{2-}] \quad (5.34)$$

$$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4 \quad (5.35) \qquad K_6 = [CaSO_4]/[Ca^{2+}][SO_4^{2-}] \quad (5.36)$$

And the complex ion formation reactions that contribute to the total soluble magnesium concentration are:

$$Mg^{2+} + OH^- \rightleftharpoons MgOH^+ \quad (5.37) \qquad K_7 = [MgOH^+]/[Mg^{2+}][OH^-] \quad (5.38)$$

$$Mg^{2+} + HCO_3^- \rightleftharpoons MgHCO_3^+ \quad (5.39) \qquad K_8 = [MgHCO_3^+]/[Mg^{2+}][HCO_3^-] \quad (5.40)$$

$$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3 \quad (5.41) \qquad K_9 = [MgCO_3]/[Mg^{2+}][CO_3^{2-}] \quad (5.42)$$

$$Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4 \quad (5.43) \qquad K_{10} = [MgSO_4]/[Mg^{2+}][SO_4^{2-}] \quad (5.44)$$

These reactions can be used to determine the effect of complex ion formation on calcium carbonate and magnesium hydroxide solubility by writing mass balance relationships for total residual calcium and total residual magnesium that consider these species. Such relationships have the form:

$$[Ca]_1 = [Ca^2] + [CaOH^+] + [CaHCO_3^+] + [CaCO_3] + [CaSO_4] \qquad (5.45)$$

That reduces to:

$$[\boldsymbol{Ca}]_{\boldsymbol{T}} = \frac{\boldsymbol{K_{sp}}}{\boldsymbol{\alpha_2 C_T}}\left(\boldsymbol{1} + \frac{\boldsymbol{K_w K_3}}{[\boldsymbol{H^+}]} + \boldsymbol{K_4 \alpha_1 C_T} + \boldsymbol{K_5 \alpha_2 C_T} + \boldsymbol{K_6}\left[\boldsymbol{SO_4^{2-}}\right]\right) \qquad \textbf{(5.46)}$$

And:

$$[\boldsymbol{Mg}]_{\boldsymbol{1}} = [\boldsymbol{Mg^2}] + [\boldsymbol{MgOH^+}] + [\boldsymbol{MgHCO_3^+}] + [\boldsymbol{MgCO_3}] + [\boldsymbol{MgSO_4}] \qquad \textbf{(5.47)}$$

Then:

$$[\boldsymbol{Mg}]_{\boldsymbol{T}} = \frac{\boldsymbol{K_{sp}}[\boldsymbol{H^+}]^2}{(\boldsymbol{K_w})^2}\left(\boldsymbol{1} + \frac{\boldsymbol{K_2 K_7}}{[\boldsymbol{H^+}]} + \boldsymbol{K_8 \alpha_1 C_T} + \boldsymbol{K_9 \alpha_2 C_T} + \boldsymbol{K_{10}}\left[\boldsymbol{SO_4^{2-}}\right]\right) \qquad \textbf{(5.48)}$$

Previously, it has been talking about the representation of hardness with bar diagrams. Two different possibilities with the concentrations of calcium and bicarbonates in these bar diagrams can be seen:

1) $[Ca^{2+}] < [HCO_3^-]$ → The calcium concentration is bigger than bicarbonate concentration and only a one step treatment (lime addition) to remove hardness is needed. When lime is added the pH raises and convert bicarbonate ions into carbonate ions and all the calcium can react with carbonate and form calcium carbonate and magnesium precipitate as magnesium hydroxide.
2) $[Ca^{2+}] > [HCO_3^-]$ → The calcium concentration is lower than bicarbonate concentration and a two-steps precipitation (lime and soda ash addition) is needed to remove hardness. In first step, when lime is added, only one part of calcium react with all carbonate and form calcium carbonate and magnesium can precipitate as magnesium hydroxide. In the second step, soda ash is added, reacting with the remaining calcium and forming more calcium carbonate.

These two cases are shown in the bar diagrams (Figure 5.3 and Figure 5.4). When the box of calcium is shorter than the bicarbonate box, one step is needed. When the calcium box is larger than bicarbonate box, the two-steps treatment is needed.

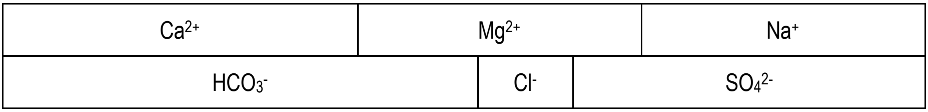


Figure 5.3 Bar diagram where calcium concentration is smaller thant bicarbonate concentration [Self production]

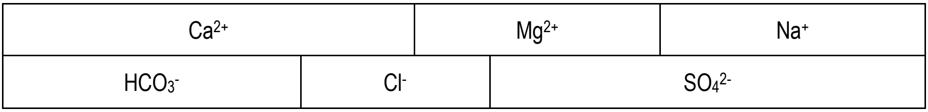


Figure 5.4 Bar diagram where calcium concentration is bigger than bicarbonate concentration [Self production]

Carbonate hardness can be removed by adding hydroxide ions (elevation the solution pH) so that the bicarbonate ions are converted into the carbonate ions (pH above 10). However, before the solution can be changed significantly, the free carbon dioxide or carbonic acid must be neutralized. The increase in the carbonate concentration from the conversion of bicarbonate to carbonate causes the calcium and carbonate ion product ($[Ca^{2+}]$ $[CO_3^{2-}]$) to exceed the solubility product constant for $CaCO_{3(s)}$, and precipitation occurs. The result is that the concentration of calcium ions, originally treated as if they were associated with the bicarbonate anions, is reduced to a lower value. The remaining dissolved calcium (non-carbonated hardness), however, can be removed by a simple pH adjustment. Then, soda ash must be added to precipitate this calcium. Carbonate and non-carbonated magnesium hardness are removed by increasing the hydroxide ion concentration until the magnesium and hydroxide ion product ($[Mg^{2+}]\cdot[OH^-]_2$) exceeds the solubility product constant for $Mg(OH)_{2(s)}$ and precipitation occurs.

pH

In order to produce calcium carbonate and magnesium hydroxide, the pH of the water must be raised by the addition of lime. Calcium compounds in water will be removed at a pH of about 9.0 to 9.5 while magnesium compounds require a pH of 10.0 to 10.5 [17, 21]. When soda ash is used to remove noncarbonated hardness, an even higher pH is require, 10.0 to 10.5 for calcium compounds and 11.0 to 11.5 for magnesium compounds [17, 21].

In this process, lime is added to provide the hydroxide ions required to elevate the pH while sodium carbonate is added to provide an external source of carbonate ions. The lime and soda ash softening process can be explained with some reactions in different steps [4, 21].

Lime-Soda Ash Softening

The first step in lime soda softening is the addition of lime to water using a typical dry feeder, either volumetric or gravimetric. Lime reacts with substances in the water before it can begin softening the water.

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_{3(s)} + 2H_2O \qquad \textbf{(5.49)}$$

Equation 5.49 is the neutralization reaction between lime and free carbon dioxide or carbonic acid that must be satisfied before the pH can be elevated significantly. Although no net change in water hardness occurs as a result of this reaction. It must be considered because carbon dioxide or carbonic acid is the primary compound which creates a demand for lime. If both carbonic acid and lime are expressed in terms of calcium carbonate, stoichiometric coefficient ratios suggest that for each mg/L of carbonic acid (expressed as $CaCO_3$) present, 1 mg/L of lime (expressed as $CaCO_3$) will be required for neutralization.

Once the carbon dioxide demand has been met, the lime is free to react with and remove carbonate hardness from the water.

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_{3(s)} + 2H_2O \qquad \textbf{(5.50)}$$

The equation 5.50 shows that for each molecule of calcium bicarbonate present, two carbonate ions can be formed by elevating the pH. One of the carbonate ions can be assumed to react with one of the calcium ions originally present as calcium bicarbonate, while the other carbonate ion can be assumed to react with the calcium ion released from the lime molecule added to elevate the pH. In both cases calcium carbonate will precipitate. If both the calcium bicarbonate and the lime are expressed in terms of $CaCO_3$, stoichiometric coefficient ratios show that for each mg/l of calcium bicarbonate (calcium carbonate hardness) present, 1 mg/L of lime (expressed as $CaCO_3$) will be required for its removal.

Equation 5.51 represents the removal of calcium non-carbonate hardness.

$$Ca^{2+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} + Na_2CO_3 \rightarrow CaCO_{3(s)} + 2Na^+ + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} \qquad \textbf{(5.51)}$$

If the calcium non-carbonate hardness is expressed in terms of $CaCO_3$, stoichiometric coefficient ratios suggest that for each mg/L of calcium non-carbonate hardness present, 1 mg/L of sodium carbonate (expressed as $CaCO_3$) will be required for its removal.

The following reaction (5.52) is somewhat similar to the reaction with calcium, but in this case magnesium carbonate hardness is removed.

$$Mg^{2+} + 2HCO_3^- + 2Ca(OH)_2 \rightarrow 2CaCO_{3(s)} + Mg(OH)_{2(s)} + H_2O \qquad \textbf{(5.52)}$$

By elevating the pH, two carbonate ions can be formed from each magnesium bicarbonate molecule. Because no calcium is considered to be present in this reaction, enough calcium ions must be added in the form of lime to precipitate the carbonate ion as calcium carbonate before the hydroxide ion concentration can be increased to the level required for magnesium removal. The magnesium is precipitated as magnesium hydroxide. If magnesium bicarbonate and lime are expressed in terms of $CaCO_3$, stoichiometric coefficient ratios state that for each mg/L of magnesium carbonate hardness present, 2 mg/L of lime (expressed as $CaCO_3$) will be required for its removal.

The next reaction (5.53) represents the removal of magnesium non-carbonate hardness.

$$\boldsymbol{Mg^{2+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} + Ca(OH)_2 \rightarrow Mg(OH)_{2(s)} + Ca^{+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix}} \quad \textbf{(5.53)}$$

If the magnesium non-carbonate hardness and lime are expressed in terms of $CaCO^3$, stoichiometric coefficient ratios state that for each mg/L of magnesium non-carbonate hardness present, 1 mg/L of lime (expressed as $CaCO_3$) will be required for its removal. In this reaction, however, note that no net change in the hardness level occurs because for every magnesium ion removed, a calcium ion is added. Thus, to complete the hardness removal process, sodium carbonate must be added to precipitate this calcium and the reaction is repeated.

$$\boldsymbol{Ca^{2+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} + Na_2CO_3 \rightarrow CaCO_{3(s)} + 2Na^{+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix}} \quad \textbf{(5.54)}$$

The chemical requirements for lime soda ash softening can be summarized as follows if all constituents are expressed as equivalent $CaCO^3$: 1mg/L of lime as $CaCO^3$ will be required for each mg/L of carbonic acid (expressed as $CaCO_3$) present; 1 mg/L of lime as $CaCO_3$ will be required for each mg/L of calcium carbonate hardness present; 1 mg/L of soda ash as $CaCO_3$ will be required for each mg/L of calcium non-carbonate hardness present; 2 mg/L of lime as $CaCO_3$ will be required for each mg/L of magnesium carbonate hardness present; 1 mg/L of lime as $CaCO_3$ and 1 mg/L of soda ash as $CaCO_3$ will be required for each mg/L of magnesium noncarbonated hardness present. To achieve removal of magnesium in the form of $Mg(OH)_{2(s)}$, the solution pH must be raised to a value greater than 10.5. This will require a lime dosage greater than the stoichiometric requirement.

Lime and soda ash softening cannot produce water completely free of hardness because of the solubility of calcium carbonate and magnesium hydroxide. Thus the minimum calcium hardness can be achieved is about 30 mg/L as $CaCO_3$ and magnesium hardness is about 10 mg/L as $CaCO_3$. It's normally tolerated a final total hardness on the order of 75 to 120 mg/L as $CaCO_3$, but the magnesium content shouldn't exceed 40 mg/L as $CaCO_3$.

There are four types of lime softening processes [21]. The characteristics of the source water will establish the type of treatment process necessary for softening. Each process name is derived from the type and amount of chemical added.

- Single stage lime process: Source water has high calcium, low magnesium carbonate hardness (less than 40 mg/L as $CaCO_3$). No non-carbonate hardness.
- Excess lime process: Source water has high calcium, high magnesium carbonate hardness. No non-carbonate hardness. May be a one or two stage process.
- Single stage lime soda ash process: Source water has high calcium, low magnesium carbonate hardness (less than 40 mg/L as $CaCO_3$). Some calcium non-carbonate hardness.
- Excess lime soda ash process: Source water has high calcium, high magnesium carbonate hardness and some non-carbonate hardness. It may be a one or two stage process.

It is possible to use different operating temperatures in the lime soda ash softening:

- Cold lime softening: This precipitation softening is carried out at ambient temperatures. This is the first invented lime softener and was used for softening potable water. Cold lime softening was very popular until recently when municipalities stopped softening the potable water.
- Warm lime softening: This process operates in the temperature range of 49-60ºC. The solubility of calcium and magnesium are reduced by increased the temperature. Therefore, they are more effectively removed by warm lime softening than by cold lime softening. This process is used in industrial water treatments. This process is used to prepare feed to a demineralization system and to lower the blowdown discharge from cooling systems. In this process temperature control is critical because a bit temperature variation can cause gross carryover of the softener precipitates.
- Hot process softening is usually carried out under pressure at temperatures of 108-116ºC. At the operating temperature, hot process softening reactions go

essentially to completion. This treatment method involves the same reactions described above, except that raw water CO_2 is vented and doesn't participate in the lime reaction.

Hot process softening can also provide very good silica reduction. The silica reduction is accomplished through adsorption of the silica on the magnesium hydroxide precipitate. If there is insufficient magnesium present in the raw water to reduce silica to the desired level, magnesium compounds such as magnesium oxide, magnesium sulfate or magnesium carbonate may be used.

Lime-soda ash processes will reduced oxidized iron and manganese to about 0.05 and 0.01 ppm, respectively. Raw water organics (color-contributing colloids) are also reduced.

Lime-soda ash softening presents different advantages. The first and the most obvious is that hardness is taken out of solution. It must be taken into account that when lime is added, it increases the quantity of calcium, but this additional calcium is removed when soda ash is applied; then sodium remains in the finished water, but this sodium is not a problem because it doesn't create scaling problems. It's important to know that total dissolved solids (TDS) are reduced with this softening process; lime also precipitates the soluble iron and manganese. Furthermore, excess lime treatment provides disinfection and provides aids in coagulation for removal of turbidity. The lime soda ash process can also be used to reduce the silica concentration. When sodium aluminate and ferric chloride are added, the precipitate will include calcium carbonate and a complex with silicic acid, aluminum oxide and iron. Another advantage of this process is that lime soda ash softening is very inexpensive. Moreover, completely enclosed systems are often conveniently self-operating and low maintenance, requiring only replenishment of the chemicals used. Often times, a sophisticated operator isn't needed.

On the other hand, competing reactions, varying levels of alkalinity and other factors typically make calculation of proper chemical dosages very difficult. Therefore, frequent jar tests are necessary for confirmation of optimal treatment conditions. Overdosing can diminish the effectiveness of the treatment. Other disadvantages can be that the chemical precipitation may require working with corrosive chemicals, increasing operator safety concerns. Furthermore, the addition of treatment chemicals, especially lime, may increase the volume of waste sludge up to 50 percent. Large amounts of chemicals may need to be transported to the treatment location.

When water, especially groundwater, has a high carbon dioxide concentration, the water is often pretreated with aeration before softening begins. This aeration removes the excess carbon dioxide and lowers the lime requirements.

5.1.2. CAUSTIC SODA SOFTENING

Caustic soda (NaOH) can be used as the primary softening chemical in place of both lime and soda ash. The reaction of caustic soda with carbon dioxide, and carbonate and non-carbonate hardness are:

$$CO_2 + 2NaOH \rightleftharpoons Na_2CO_3 + H_2O \quad \textbf{(5.55)}$$

$$Ca(HCO_3)_2 + 2NaOH \rightleftharpoons CaCO_3 + Na_2CO_3 + H_2O \quad \textbf{(5.56)}$$

$$Mg(HCO_3)_2 + 4NaOH \rightleftharpoons Mg(OH)_2 + 2Na_2CO_3 + H_2O \quad \textbf{(5.57)}$$

$$MgSO_4 + 2NaOH \rightleftharpoons Mg(OH)_2 + Na_2SO_4 \quad \textbf{(5.58)}$$

Caustic soda removes the free carbon dioxide and carbonate hardness, producing calcium carbonate, which precipitates, and soluble sodium carbonate. It also reacts with non-carbonate hardness, producing magnesium hydroxide, which precipitates. The above equations demonstrate that caustic soda can remove both carbonate and non-carbonate hardness. It can not only take the place of soda ash, but can satisfy all or a part of the lime requirement as well. The advisability of using caustic soda as a softening chemical depends on the comparative costs of lime, soda ash and caustic soda in the area. Usually caustic soda will not be very competitive [20].

5.2. ION EXCHANGE

Ion exchange is a separating operation based on solid-liquid mass transfer. This process involves the transfer of one or more ions from the fluid phase to the solid phase by ion exchange or displacement of the same charge ions. These ions are connected by electrostatic forces to superficial functional groups. The process efficiency depends on the solid-liquid equilibrium and the rate of mass transfer. The solids are usually polymers. The most common are the synthetic resins. An ion exchange resin can be considered as a structure of hydrocarbon chains that are rigidly connected with free ionic groups. These chains are transversally joined to form a three dimensional matrix which provides rigidity to the resin. The crosslinking degree establishes the internal pore structure of the resin. There are two different types of resins; cationic and anionic resins [2, 21, 22, 23].

Ionizable groups attached to the resin beads determine the functional capability of the resin. Industrial water treatment resins are classified into four basic categories [21]:

- *Strong acid cation resins* can neutralize strong bases and convert neutral salts into their corresponding acids.
- *Strong bases anion resins* can neutralize strong acids and convert neutral salts into their corresponding bases. These resins are utilized in most softening and full demineralization applications
- *Weak acid cation resins* and *weak base anion resins* are able to neutralize strong bases and acids, respectively. These resins are used for dealkalization, partial demineralization or (in combination with strong resins) full demineralization.

Sodium zeolite softening is the most widely applied use of ion exchange. In zeolite softening, water containing scale-forming ions, such as calcium and magnesium, passes through a resin bed containing strong acid cation resin in the sodium form. In the resin, the hardness ions are exchanged with the sodium diffuses into the bulk water solution.

Calcium and magnesium ions are atoms having a positive electrical charge, as do sodium ions. Ions of the same charge can be exchanged. In this ion exchange process, a resin that is coated with sodium ions (non-hardness ions) comes into contact with water containing calcium and magnesium ions. Two positively charged sodium ions are exchanged (released into the water) for every calcium or magnesium ion that is held by the resin. This exchange happens because sodium is loosely held by the resin. In this way, calcium and magnesium ions responsible for hardness are removed from the water, held by the resin, and replaced by sodium ions in water. These sodium ions don't generate any hardness to the water. This resins exchange cations and are functional at any pH value.

The softening process with ion exchange and the recharging process of the resin when this is exhausted can be seen in the Figure 5.5.

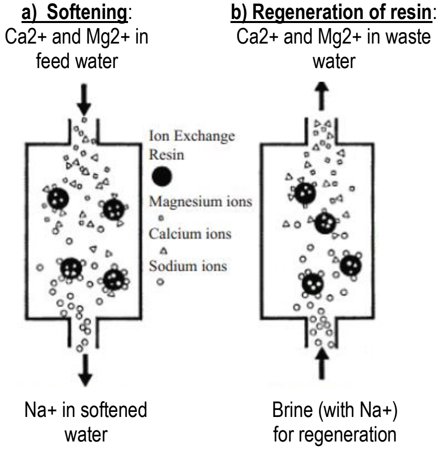


Figure 5.5 Ion Exchange process (a) and regeneration process (b) [Adapted from Skipton S. O. Ref.23]

Eventually, a point is reached when very few sodium ions remain on the resin, thus no more calcium or magnesium ions can be removed from the raw water. The resin at this point is said to be exhausted or spent, and must be recharged or regenerated.

The process of ion exchange to soften water can be show in equation 5.59:

$$\boldsymbol{\underset{(with\ Ca^{2+}\ and\ Mg^{2+})}{Hard\ Water} + \underset{(with\ Na^{+})}{Resin} \rightarrow \underset{(with\ Na^{+})}{Soft\ Water} + \underset{(with\ Ca^{2+} and\ Mg^{2+})}{Resin}} \tag{5.59}$$

And:

$$\boldsymbol{R < \frac{Na}{Na} + Ca^{2+} \rightarrow R = Ca + 2Na^{+}} \tag{5.60}$$

When the resin is exhausted or spent, it’s necessary to recharge it. The process to recharge the resin is the reverse operation. A concentrate solution of sodium chloride passes through the resin and all sodium ions that are in the water, replace the calcium and magnesium ions on the exhausted resin bed. The resin returns at his original form and is ready to be used again. It’s also used hydrochloric acid or sulfuric acid, but there are more expensive than sodium chloride. The resin can be regenerated many times before to be renewed. During regeneration, a large excess of regenerant (approximately 3 times the amount of calcium and magnesium in the resin) is used [21].

After regeneration, small residual amounts of hardness remain in the resin. If the resin remains in a stagnant vessel of water, some hardness will diffuse into the raw water. Therefore, at the initiation of flow, the water effluent from a zeolite softener can contain hardness even if it has been regenerated recently. After a few minutes of flow, the hardness is rinsed from the softener, and the treated water is soft.

The regeneration process can be show in following equation:

$$\boldsymbol{\begin{array}{c}\mathit{Sodium\ chloride\ solution}\\(\mathit{with}\ Na^{+})\end{array} + \begin{array}{c}\mathit{Inactive\ Resin}\\(\mathit{with}\ Ca^{2+}\mathit{and}\ Mg^{2+})\end{array} \rightarrow \begin{array}{c}\mathit{Reject\ Water}\\(\mathit{with}\ Ca^{2+}\mathit{and}\ Mg^{2+})\end{array} + \begin{array}{c}\mathit{Recharged\ Resin}\\(\mathit{with}\ Na^{+})\end{array}} \qquad \mathbf{(5.61)}$$

The regeneration or recharge cycle frequency depends on the hardness of the water, the amount of water used, size of the softener, and capacity of the resins. It’s important to know that the life of the resin can be very short if the water is feed with a lot of suspended solids. These solids close the orifices of the resin. To avoid this situation, a filtration system is used as a pre-treatment to the ion exchange process.

Ion exchange softening is a good process to soften water because the water treated has a very slow scaling tendency because this method reduces the hardness level of most water supplies to less than 2 ppm. Furthermore, the operation is simple and reliable and salts are cheap and easy to handle.

Although sodium zeolite softeners efficiency reduces the amount of dissolved hardness in a water supply, the total solids content and alkalinity in water remain unaffected. Plants that have replaced their hot process softeners with only zeolite softeners have experienced problems with silica and alkalinity in their boilers. In addition, the resin can be fouled by heavy metal contaminants, such as iron and aluminum which are not removed during the course of a normal regeneration. If excess iron or manganese is present in the feed water, the resin must be cleaned periodically. It's important to take into account that this process produces high amount of effluent due to regeneration process. Then, these effluents have to be treated and it produces additional costs.

5.3. MEMBRANE SOFTENING

Membrane technology has made a lot of progresses in last years. Membrane softening is a term applied to a water treatment process that uses nanofiltration (NF) membrane technology to reduce hardness and remove organics and other impurities from the raw water. Nanofiltration is often referred to as modified reverse osmosis (RO) because it is based on very similar operating principles. Nanofiltration is a pressure-driven separation process that employs a semipermeable membrane and the principles of size exclusion and solution-diffusion to split a feed water stream into two parts. A purified “permeate” water stream and a waste “concentrate” stream containing a high percentage of the impurities found in the raw water. The membrane is a film that allows the water and the small ions to pass through it and rejects large ions such as Ca^{2+}, Mg^{2+}, Fe^{3+}. The nanofiltration permeate is water with small ions such as Na^{+}, K^{+}, Cl^{-} and free of hardness. The concentrate contains almost all large ions that cause water hardness [2, 20, 21, 22, 24].

Membrane softening using nanofiltration membranes is an option when very high level of salt rejection is not necessary or even desirable (reverse osmosis has higher rejection than NF but has higher pressure requirement and more expensive investment and operation costs). Nanofiltration membranes partially soften water, removing between 10% and 90% of dissolved salts compared to up to 99.5% for reverse osmosis.

Nanofiltration membranes need a periodic cleaning and a maintenance strategy to have the membranes in optimum conditions.

Most of the polymeric NF membranes used are nonporous cross-linked network structures with the presence of an ionic group. The term “thin film composite” (TFC) is often used. The TFC membrane with polyamide and polysulfone allows high production with low pressure and better quality of water produced [25].

The life of the membranes is between five and eight years, but this is only indicative. The lifespan of a membrane is highly dependent maintenance during operation. But for the softening application, the membrane life is really reduced, because hard water that is treated cause scaling in the membrane [21].

Nanofiltration is also a highly cost-effective option when is compared with lime softening [25]. The installation cost for nanofiltration or lime softening at same capacity is about the similar, but membrane plant expansions are easier and less expensive than expansions of lime softening facilities. What's more, because lime softening capacity must be installed in large increments, it is often necessary to install and pay for excess capacity in advance to accommodate projected growth in demand. Membrane technology, on the other hand, is adaptable to any plant size and its modularity allows any plant capacity expansion. Operating costs for membrane softening plants are often lower than for lime softening facilities, too. Also contributing favorably to the cost advantages of membrane softening are the reduce land requirements involved. Membrane plants require about one-third of the space of lime softening plants. The membrane filtration has more control about the filtrate quality because in the membrane surface the particle size is more regular and efficient.

A disadvantage of membrane softening processes is the fouling. A backwash can be made, but the membrane never returns to its initial conditions, and it's impossible to maintain the efficiency of the first day [25].

5.4. ELECTRODIALYSIS

Electrodialysis is a membrane process that was initially developed in the 1950s. Since then, Electrodialysis has advanced rapidly because of improved ion exchange membrane properties, better materials of construction and advances in technology. In this process an electrical potential is applied between electrodes and the ionic constituents in the water are thus caused to migrate through semi-permeable membranes which are selective to cations and anions. Electrodialysis is used on very hard water, with a hardness of more than 500 mg/L as calcium carbonate [21, 26, 27].

The membranes are cation or anion selective, which basically means that either positive or negative ions will flow through [26]:

- Cation transfer membranes are electrically conductive membranes that allow only positively charged ions to pass through. This membranes generally consists of cross-linked polystyrene that has been sulfonated to produce $–SO_3H$ groups attached to the polymer, in water this group ionizes producing a mobile counter ion (H^+) and a fixed charge ($-SO_3^-$).
- Anion transfer membranes are electrically conductive membranes that allow only negatively, charged ions to pass through. Usually, the membrane matrix has fixed positive charges from quaternary ammonium groups ($-NR_3^+OH^-$) which repel positive ions.

This technique can be applied to remove salts and other ionized species. Particles that don't carry an electrical charge are not removed. Electrodialysis removes dissolved solids, based on their electrical charge, by transferring the brackish water ions through a semi-permeable ion exchange membrane charged with an electrical potential. It points that the feed water becomes separated into the following three types of water [26]:

- Product water, which has an acceptably amount of calcium and magnesium, low conductivity and TDS level.
- Brine or concentrate, which is the water that receives the brackish water ions.
- Electrode feed water, which is the water that passes directly over the electrodes that create the electrical potential.

Reverse electrodialysis is a variation on the electrodialysis process, which uses electrode polarity reversal to automatically clean membrane surfaces. Reverse electrodialysis works the same way as electrodialysis, except that the polarity of the direct current power is reversed two to four times per hour. When polarity is reversed, the source water dilute and concentrate compartments are also reversed and so are the chemical reactions at the electrodes. This polarity reversal helps prevent the formation of scale on the membranes.

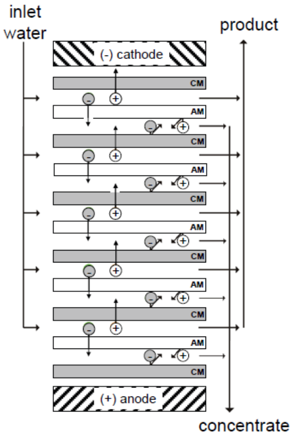


Figure 5.6 Electrodialysis process [Valero F. et al. Desalination. Trends and Technologies. Ref.26]

It could be necessary to clean the membranes periodically. Cleaning is a means of removing mineral scale or insoluble constituents which build up on the surface of the membrane. To prevent scaling and fouling, electrodialysis and reverse electrodialysis units are equipped with a clean-in-place system to allow periodic flushing of the membrane stack and piping with an acid solution.

Sometimes a pretreatment is necessary before the Electrodialysis can take place. Suspended solids with a diameter that exceeds 10 µm need to be removed, or else they will plug the membrane pores. There are also substances that are able to neutralize the membrane, such as large organic anions, colloids, iron oxides and manganese oxide. These disturb the selective effect of the membrane. The pretreatment methods which aid the prevention of these effects are active carbon filtration (for organic matter), flocculation (for colloids) and filtration techniques [27].

6. CHEMICAL SPECIATION SOFTWARE

A chemical speciation software have been used in this project to simulate water softening by chemical precipitation with different types of waters. The chemical speciation software is the OLI Studio Analyzer®, which will be described in this section.

The OLI Studio Analyzer® (OLI from now) is a computer software used for simulating aqueous-based chemical systems developed by OLI Systems Inc. OLI is a single- and multiple-point chemical calculator. Its basic action is to calculate the equilibrium properties of user-entered inflows (e.g. $CaCO_3$, $Mg(OH)_2$) and conditions (T, P).

This software utilizes a predictive thermodynamic framework for calculating the physical and chemical properties of multiphase, aqueous-based systems. The thermodynamic framework is applicable to multicomponent mixtures of chemicals in water, and is predictive over a wide range of temperature, pressure and concentration of interest. Supported by an in-place databank, the software allows users to predict the chemical and phase behavior of mixtures of inorganic or organic chemicals in water [28].

OLI has developed a theoretical frameworks, database, data regression techniques, and applications software that comprehensively and accurately simulate and predict chemical systems. It is based in the following elements [29]:

- The OLI model predicts and considers all of the true species in solution, and accounts for these in the computations.
- Based on the Helgeson equation of state and parameter regression and proprietary estimation techniques, the OLI model provides accurate equilibrium constants and other standard state properties over the broadest possible aqueous range of conditions.
- OLI models can predict behavior under real conditions.
- The OLI Databank covers 80 inorganic elements and their associated compounds and complexes, and over 8000 organic chemicals.
- OLI has developed a chemical-physical based models to compute thermodynamic and transport properties for complex aqueous mixtures.

The evaluation of the standard-state Gibbs Free Energy equation (6.1) is central to the OLI software [30].

$$\Delta_R \overline{G}^0 = -RTlnK \qquad \textbf{(6.1)}$$

Where $\Delta_R G^0$ is the partial molal, standard-state Gibbs Free Energy of Reaction, R is the Gas Constant (8,314 J/mole/K), T is the temperature (Kelvin) and K is the equilibrium constant.

OLI defines $\Delta_R G^0$ as:

$$\Delta_R \overline{G}^0 = \sum_i \nu_i \Delta_f \overline{G}_i(PRODUCTS) - \sum_i \nu_i \Delta_f \overline{G}_i(REACTANTS) \qquad \textbf{(6.2)}$$

Where v_i is the Stoichiometric coefficient and ∆Gi is the Gibbs Free Energy of Formation for a species. This refers (6.2) to the total free energy, not just the standard-state portion.

Each thermodynamic property is composed of two parts. The first is the standard state part which is only a function of temperature and pressure (denoted by the superscript ^{0}). The second is the excess part which is a function of temperature and pressure as well as concentration (denoted by the superscript ^{E}) [30].

Partial Molal Gibbs Free Energy (6.3)

$$\overline{G}_i = \overline{G}_i^0 + \overline{G}_i^E \qquad \textbf{(6.3)}$$

Partial Molal Enthalpy (6.4)

$$\overline{H}_i = \overline{H}_i^0 + \overline{H}_i^E \qquad \textbf{(6.4)}$$

Partial Molal Entropy (6.5)

$$\overline{S}_i = \overline{S}_i^0 + \overline{S}_i^E \qquad \textbf{(6.5)}$$

Partial Molal Heat Capacity (6.6)

$$\overline{C}p_i = \overline{C}p_i^0 + \overline{C}p_i^E \qquad \textbf{(6.6)}$$

Partial Molal Volume (6.7)

$$\overline{V}_i = \overline{V}_i^0 + \overline{V}_i^E \qquad \textbf{(6.7)}$$

Working since 1968, Helgeson [30] have found that the standard-state thermodynamic property of any species in water can be represented by a function with seven terms which have specific values for each species. The seven terms (a_1, a_2, a_3, a_4, c_1, c_2 and ω) are integration constants for volume (a), heat capacity (c) and temperature and pressure properties of water (ω). They are independent of the data system used to obtain them.

$$\overline{H}_i^0 = \overline{H}_i^R + f_{Hi}(a_1, \dots, a_4, c_1, c_2, \omega) \tag{6.8}$$

$$\overline{G}_i^0 = \overline{G}_i^R - \overline{S}_i^R(T - T^2) + f_{Gi}(a_1, \dots, a_4, c_1, c_2, \omega) \tag{6.9}$$

$$\overline{S}_i^0 = \overline{S}_i^R + f_{Si}(a_1, \dots, a_4, c_1, c_2, \omega) \tag{6.10}$$

$$\overline{C}p_i^0 = \overline{C}p_i^R + f_{Cpi}(a_1, \dots, a_4, c_1, c_2, \omega) \tag{6.11}$$

$$\overline{V}_i^0 = \overline{V}_i^R + f_{Vi}(a_1, \dots, a_4, c_1, c_2, \omega) \tag{6.12}$$

The Helgeson Equation of State [30] of each property are the followings:

Enthalpy (6.13):

$$\Delta\overline{H_{P,T}^0} = \Delta\overline{H_f^0} + c_1(T - T_r) - c_2\left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right] + a_1(P - P_r) + a_2 ln\left(\frac{\Psi+P}{\Psi+P_r}\right) +$$

$$+\left(a_3(P - P_r) + a_4 ln\left[\frac{\Psi+P}{\Psi+P_r}\right]\right)\left[\frac{2T-\Theta}{(T-\Theta)^2}\right] + \omega\left(\frac{1}{\varepsilon} - 1\right) + \omega TY - T\left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\delta\omega}{\delta T}\right)_P +$$

$$-\omega_{Pr,Tr}\left(\frac{1}{\varepsilon_{Pr,Tr}} - 1\right) - \omega_{Pr,Tr}T_\gamma T_\gamma \tag{6.13}$$

Gibbs Free Energy (6.14):

$$\Delta\overline{G_{P,T}^0} = \Delta\overline{G_f^0} - \overline{S_{Pr,Tr}^0}(T - T_r)\left[T ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(P - P_r) + a_2 ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\left(\frac{\Psi+P}{\Psi+P_r}\right) +$$

$$+\left[a_3(P - P_r) + a_4 ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]\left(\frac{1}{T-\Theta}\right) - c_2\left[\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right)\left(\frac{\Theta-T}{\Theta}\right) - \frac{T}{\Theta^2} ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right] +$$

$$+\omega\left(\frac{1}{\varepsilon} - 1\right) - \omega_{Pr,Tr}\left(\frac{1}{\varepsilon_{Pr,Tr}} - 1\right) + \omega_{Pr,Tr}Y_{Pr,Tr}(T - T_r) \tag{6.14}$$

Volume (6.15):

$$\overline{V^0} = a_1 + a_2\left(\frac{1}{\Psi+P}\right) + \left[a_3 + a_4\left(\frac{1}{\Psi+P}\right)\right]\left(\frac{1}{T-\Theta}\right) - \omega Q + \left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\delta\omega}{\delta P}\right)_T \tag{6.15}$$

Heat Capacity at Constant Pressure (6.16):

$$\overline{Cp^0} = c_1 + c_2\left(\frac{1}{T-\Theta}\right)^2 - \left(\frac{2T}{(T-\Theta)^3}\right)\left[a_3(P - P_r) + a_4 ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right] +$$

$$+\omega TX + 2TY\left(\frac{\delta\omega}{\delta P}\right)_T - T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\delta^2\omega}{\delta T^2}\right)_P \tag{6.16}$$

Entropy (6.17):

$$\overline{S^0} = \overline{S^0_{Pr,Tr}} + c_1 ln\frac{T}{T_t} - \frac{c_2}{\Theta}\left\{\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right) + \frac{1}{\Theta} ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right\} +$$

$$+\left(\frac{1}{T-\Theta}\right)^2\left[a_3(P-P_r) + a_4 ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right] + \omega Y - \left(\frac{1}{\varepsilon}-1\right)\left(\frac{\delta\omega}{\delta P}\right)_T - \omega_{Pr,Tr}Y_{Pr,Tr}$$

(6.17)

With the excess properties, the concept of activities and activity coefficients is introduced.

OLI Studio Analyzer is based in a mathematic model. This is many mathematical formulas to express relations, variables, parameters and their relationships. Also express some operations to study the behavior of systems. This software uses two different models to calculate thermodynamics parameters; aqueous model and mixed solvent electrolyte model [28, 29].

6.1. AQUEOUS (AQ) MODEL

OLI's basic electrolyte thermodynamic model – the aqueous model – is based on a true speciation model, a predictive equation of state (Helgeson equation-of-state), an activity coefficient model, and convergence heuristics. The OLI aqueous model covers more than 80 elements of the periodic table. The model is based upon published experimental data. The model uses data regression wherever possible and estimation and extrapolation where required. It is based on the empirical extensions of the initial Debye-Hückel model. Aqueous model provides general simulation capability giving accurate prediction for almost any water chemistry mixture over the range [28]:

Water Content: >65% (molar)

Temperature: -50 to 300ºC

Pressure: 0 to 1500 bar

Ionic Strength: 0 to 30 molal

The aqueous model (Standard Chemistry Model) is based on the standard-state properties using the Helgeson equation-of-state and excess properties using the aqueous activity coefficient expressions developed by Debye-Hückel, Bromley and Bromley-Zemaitis. [31]

The Debye-Hückel model assumes that only electrostatic forces act between ions and that every ion is surrounded by other ions of the total charge equal to that of the central ion (6.18).

$$\boldsymbol{log\gamma_{\mp} = -\frac{A|z_+z_-|\sqrt{I}}{1+\beta a\sqrt{I}}} \qquad \textbf{(6.18)}$$

Where A is the Debye-Hückel Constant, I is the Ionic Strength, $\boldsymbol{\gamma}$ is mean activity coefficient, z_+ is the charge of the cation and z_- is the charge of the anion.

In 1973 Bromley introduced a modification of the β coefficient of the Debye-Hückel model (6.19). The coefficient was replaced by the Bromley coefficient, B.

$$\boldsymbol{log\gamma_{\mp} = -\frac{A|z_+z_-|\sqrt{I}}{1+\beta a\sqrt{I}} + \frac{(0.06+0.6B)|z_+z_-|I}{\left(1+\frac{1.5}{z_+z_-}I\right)^2} + BI} \qquad \textbf{(6.19)}$$

Where B is the Bromley parameter (6.20).

$$\boldsymbol{B = B_+ + B_-} \qquad \textbf{(6.20)}$$

In Bromley-Zemaitis model, also called “Aqueous”, two other components were added. This model contains the C and D coefficients. Increase in the model accuracy was achieved with these changes (6.21).

$$\boldsymbol{log\gamma_{\mp} = -\frac{A|z_+z_-|\sqrt{I}}{1+\beta a\sqrt{I}} + \frac{(0.06+0.6B)|z_+z_-|I}{\left(1+\frac{1.5}{z_+z_-}I\right)^2} + BI + CI^2 + DI^3} \qquad \textbf{(6.21)}$$

Where C and D are new terms. Each of the B, C, and D terms have the following temperature functionality (6.22, 6.23, 6.24).

$$\boldsymbol{B = B_1 + B_2T + B_3T^2} \qquad \textbf{(6.22)}$$

$$\boldsymbol{C = C_1 + C_2T + C_3T^2} \qquad \textbf{(6.23)}$$

$$\boldsymbol{D = D_1 + D_2T + D_3T^2} \qquad \textbf{(6.24)}$$

Where T is temperature in centigrade.

The limiting factor of the aqueous (AQ) model is that it is applicable for ionic strength up to 30 mol/kg. The AQ model is a good working model within its limits. It has 38 years of development and an extensive database to support it.

6.2. MIXED SOLVENT ELECTROLYTE (MSE) MODEL

With the mixed solvent electrolyte (MSE) model, OLI removes the concentration limit. Where the AQ model is valid to a concentration limit of 30 molal ionic strength; the MSE model predicts electrolyte behavior from infinite dilution to diluted salts. The MSE model utilized all prior work on the Helgeson equation-of-state and supporting databank through a conversion of the standard-state chemical potentials provided for aqueous systems. This means that the equilibrium constants and other standard state partial molal thermodynamic properties are readily predicted for mixed solvent environments. The MSE model has a range of [28, 29]:

Water Content: 0-100% (mass)

Temperature: -50 to 300ºC

Pressure: 0 to 1500 bar

Ionic Strength: Up to pure salts (No limit)

The MSE chemistry model uses a combined equation (6.25) for a Debye-Hückel equation on a mole-fraction basis to represent the long-range electrostatic interactions (6.26). A Margules-type equation is used to represent the middle-range interactions (6.27). Short-range interactions are represented by the extended UNIQUAC local composition model that it consists of combinatorial and residual terms.

$$ln\gamma_i = ln\gamma_i^{LR} + ln\gamma_i^{MR} + ln\gamma_i^{SR} \qquad \textbf{(6.25)}$$

Where LR is long-range, MR is middle-range and SR is short-range.

$$ln\gamma_i^{LR} = -A_x\left[\frac{2z_i^2}{\rho}ln\left(\frac{1+\rho\sqrt{I_x}}{\sum_k x_k\left[1+\rho\sqrt{I_{x,k}^0}\right]}\right)+\frac{\sqrt{I_x}(z_1^2-2I_x)}{1+\rho\sqrt{I_{x,k}}}\right]+$$

$$-\frac{4A_xI_x}{\rho}\left\{ln\frac{1+\rho\sqrt{I_x}}{\sum_k x_k\left[1+\rho\sqrt{I_{x,k}^0}\right]}\left(\sum_l n_l\right)\left[\frac{1}{2\cdot d_s}\frac{\delta d_s}{\delta n_l}-\frac{3}{2\cdot\varepsilon_s}\frac{\delta\varepsilon_s}{\delta n_l}\right]-\frac{1+\rho\sqrt{I_{x,k}^0}}{\sum_k x_k\left[1+\rho\sqrt{I_{x,k}^0}\right]}+1\right\}$$

(6.26)

$$ln\gamma_i^{MR} = \sum_k\sum_j x_kx_jB_{kj}(I_x) - \left(\sum_i n_i\right)\sum_k\sum_j x_kx_j\frac{\delta B_{kj}(I_x)}{\delta n_i} - 2\sum_k x_kB_{ki}(I_x)$$

(6.27)

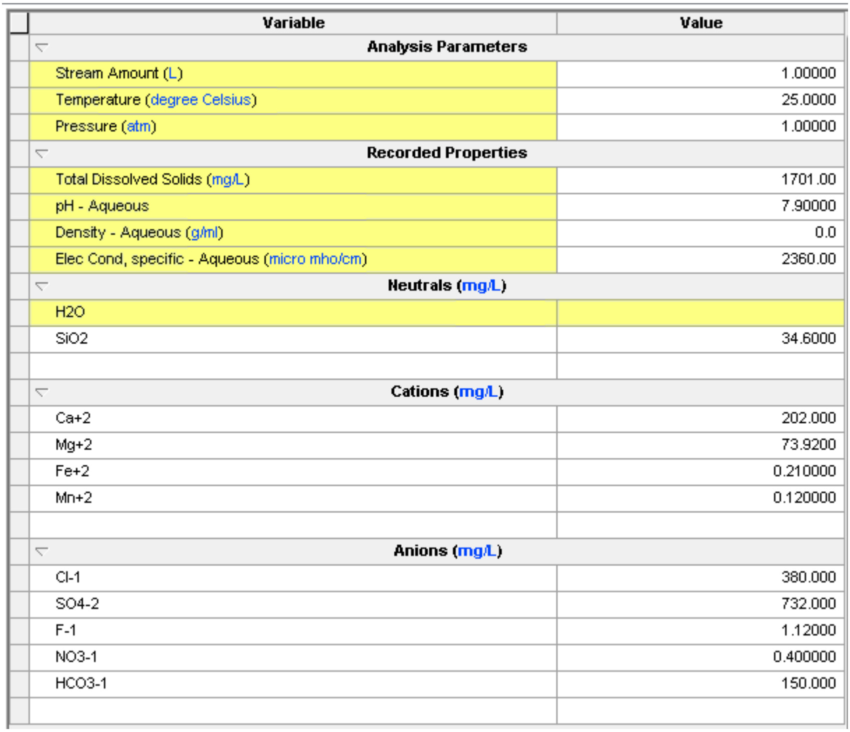
The objective of OLI's mixed solvent electrolyte (MSE) model is to produce a model capable of reproducing speciation, chemical, and phase equilibria, applicable to water-organic-salt systems in the full range of concentrations as well as aqueous electrolytes from dilute solutions to the fused salt limit.

The MSE model is a good working model for electrolytes that are highly miscible in water and that will form a second solvent.

7. MATERIALS AND METHODS

As stated in previous section, OLI is the specific software to perform chemical precipitation simulations. In this section, all ways of working with this software will be explained. The Aqueous (AQ) model is the selected model to work with OLI.

First of all, the option “WaterAnalysis” has been selected to import a stream with the composition of the feed water. All waters can be described in OLI by their ions, the temperature, the total dissolved solids, the pH and the conductivity. Then, a reconciliation must be done to comply the electroneutrality in the water (see Figure 7.1). The yellow boxes can’t be modified and in the white boxes the values can be introduced and modified. In this part, OLI calculate the different aqueous, vapor, and solid species that may be in the inflow stream.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (degree Celsius)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	1701.00
pH - Aqueous	7.90000
Density - Aqueous (g/ml)	0.0
Elec Cond, specific - Aqueous (micro mho/cm)	2360.00
Neutrals (mg/L)	
H2O	
SiO2	34.6000
Cations (mg/L)	
Ca+2	202.000
Mg+2	73.9200
Fe+2	0.210000
Mn+2	0.120000
Anions (mg/L)	
Cl-1	380.000
SO4-2	732.000
F-1	1.12000
NO3-1	0.400000
HCO3-1	150.000

Figure 7.1 Framework of introduction of water composition [Self production]

The more information of the physic-chemical characteristics of water the better the definition made for the calculation by OLI.

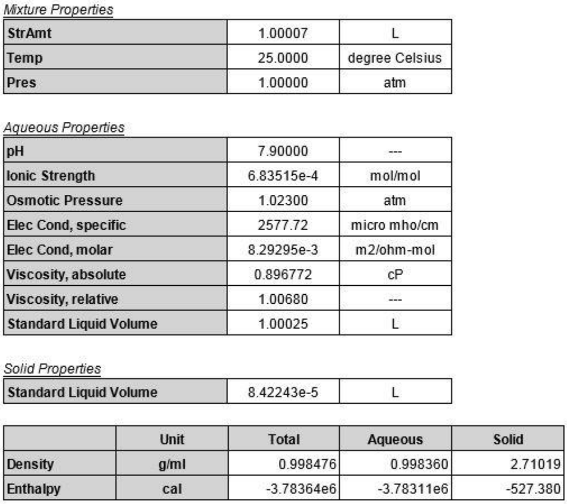
Now, the option of “No Reconcile”, “Reconcile pH” or “Reconcile pH/Alkalinity” can be selected. Usually, the option selected will be “Reconcile pH”, because it is an important parameter to define. OLI always calculates an estimated value of pH but the correct value is exposed in water analysis, the difference can be caused by an approximate water analysis. With this option different specifications have been defined. pH adjustment in OLI is made by adding a titrant (acid or base) to move the value of pH to the desired value. Normally, NaOH or HCl are chosen to increase or decrease the pH, because they provide ions that don’t cause hardness. In addition, OLI makes an electroneutrality balance. If the result of this balance between anion charge and anion charge gives an imbalance, NaOH or HCl will be added to keep balanced the electroneutrality.

Once the reconciliation is finished, the ionic composition of the water is exposed as a molecular basis at given temperature, pressure and pH. Then this molecular basis can be exported as a stream (Figure 7.2).

Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00007
Temperature (degree Celsius)	25.0000
Pressure (atm)	1.00000
Molecular Totals (mg/L)	
CaCl2	352.869
CaCO3	183.249
CaF2	2.30119
CO2	27.6057
FeCl2	0.476594
H2O	9.96456e5
MgCl2	206.935
MgO	34.9723
MnCl2	0.274860
N2O5	0.348370
NaOH	566.702
SiO2	34.5977
SO3	610.044

Figure 7.2 Molecular Basis of Introduced Water [Self production]

As a stream, many simulations and calculations can be performed. The next step is the addition of a calculation, in this case, a “Single Point” (the most common in OLI). “Single Point” computes the properties for a stream at one set of conditions. There are a lot of options with a “Single Point” calculation like isothermal calculations, isenthalpic calculations, determination of the bubble point, the dew point, the vapor amount or the vapor fraction, and the precipitation point. OLI exposed a report with different properties of the input water such as ionic strength, osmotic pressure, viscosity, density or enthalpy (Figure 7.3).



Mixture Properties

StrAmt	1.00007	L
Temp	25.0000	degree Celsius
Pres	1.00000	atm

Aqueous Properties

pH	7.90000	---
Ionic Strength	6.83515e-4	mol/mol
Osmotic Pressure	1.02300	atm
Elec Cond, specific	2577.72	micro mho/cm
Elec Cond, molar	8.29295e-3	m2/ohm-mol
Viscosity, absolute	0.896772	cP
Viscosity, relative	1.00680	---
Standard Liquid Volume	1.00025	L

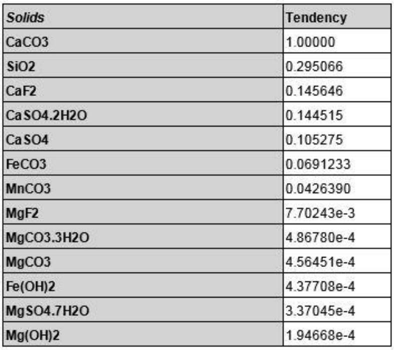
Solid Properties

Standard Liquid Volume	8.42243e-5	L

	Unit	Total	Aqueous	Solid
Density	g/ml	0.998476	0.998360	2.71019
Enthalpy	cal	-3.78364e6	-3.78311e6	-527.380

Figure 7.3 Reported properties of input stream [Self production]

It also shows the scaling tendencies (Figure 7.4). The scaling tendencies are the ratio of the real-solution solubility product to the thermodynamic limit based on the thermodynamic equilibrium constant.

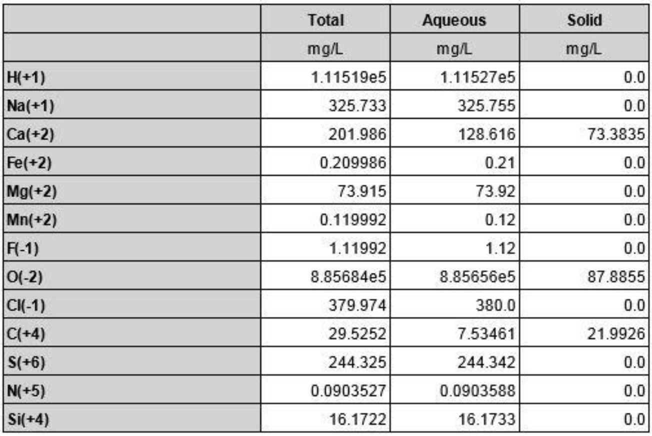


Solids	Tendency
CaCO3	1.00000
SiO2	0.295066
CaF2	0.145646
CaSO4.2H2O	0.144515
CaSO4	0.105275
FeCO3	0.0691233
MnCO3	0.0426390
MgF2	7.70243e-3
MgCO3.3H2O	4.86780e-4
MgCO3	4.56451e-4
Fe(OH)2	4.37708e-4
MgSO4.7H2O	3.37045e-4
Mg(OH)2	1.94668e-4

Figure 7.4 Reported scaling tendencies of input stream [Self production]

Furthermore, OLI reports an elemental balance with the amounts of all the ions in the input water and in which phase they are (Figure 7.5). “Single Point” is very useful to determine different properties of the waters and gives a broad overview of the defined system.

In the “Isothermal Single Point”, an isothermal calculation is pre-defined to give composition at a fixed temperature and pressure. It is the “StreamAnalyzer” simplest calculation and the most used simulation of this project. The precipitated amount of calcium carbonate and magnesium hydroxide will be checked at elemental balance of the “Single Point”.



	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11519e5	1.11527e5	0.0
Na(+1)	325.733	325.755	0.0
Ca(+2)	201.986	128.616	73.3835
Fe(+2)	0.209986	0.21	0.0
Mg(+2)	73.915	73.92	0.0
Mn(+2)	0.119992	0.12	0.0
F(-1)	1.11992	1.12	0.0
O(-2)	8.85684e5	8.85656e5	87.8855
Cl(-1)	379.974	380.0	0.0
C(+4)	29.5252	7.53461	21.9926
S(+6)	244.325	244.342	0.0
N(+5)	0.0903527	0.0903588	0.0
Si(+4)	16.1722	16.1733	0.0

Figure 7.5 Reported elemental balance of input water. Solid Ca(2+), O(-2) and C(4+) represent the precipitated $CaCO_3$ [Self production]

Other used “Single Point” in this project is to calculate a precipitation point. A precipitation or solubility point calculation computes the amount of the material held in solution at a given temperature and pressure able to precipitate.

Three “Single Point” will be performed in each water simulation. The first “Single Point” will be done initially to check the composition of feed water comparing with the analytical data. The second will be done after the simulation to find out the lime dosage (first step of softening). The last “Single Point” will be done at the end of the simulation to check the soda ash dose (second step of softening).

The “Survey” is the necessary calculation to find out the lime and soda ash dosage in a simulation. In a “Survey”, the changes experienced by the addition of a specific chemical and the modification of their properties will be analyzed. “Survey” can be described as a series of

"Single Point" calculations in which independent variable such as temperature or composition varies with each calculation. Up to two variables can be adjusted simultaneously, and a third can be fixed. There are different types of "Survey", by temperature, by pressure, by composition or by pH.

Determine the effect of adding a species to feed water is possible with a "Survey" by composition. In this framework is necessary to define a compound to add in the feed water. A "Survey Range" has to be defined. Usually, it starts at the 0 point and the end point is defined by the user (i.e. x mg/L of the added chemical). Furthermore, the increment or the number of steps has to be specified. Then the calculation is possible.

Results can be analyzed in a customizable plot or graphic. This graphic shows the evolution of the system to each step, between 0 to the set end point. The "Survey" also has a full and also customizable report in tables with the same information of the "Single Point" calculation, but now, for each step of the "Survey".

Two "Survey" will be done in each simulation of feed water. The first "Survey" is necessary to define the lime dosage. With this "Survey" a plot is obtained (Figure 7.6).

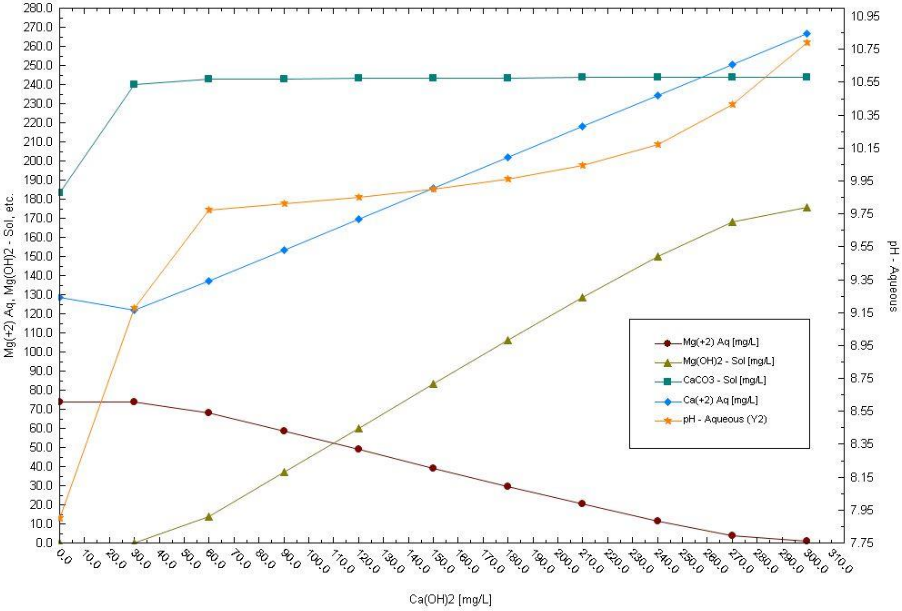


Figure 7.6 Plot obtained after "Survey" by composition of lime addition [Self production]

It is important to know that all the graphics exposed in this project will follow the same pattern. In the abscissa axis of the graphical representation the lime dosage can be seen. The left ordinate axis represents the concentration in mg/L of different compounds in the water. The right ordinate axis shows the pH of the water. It is possible to see that when the lime dosage starts there is a small precipitation of calcium (blue line), therefore, the amount of calcium carbonate rises (green line). Then the magnesium starts to precipitate up to zero (brown line), hence the magnesium hydroxide rises until there isn't more magnesium in water to precipitate (olive line). The orange line represents the evolution of the pH during the lime addition.

The interpretation given to the simulated lime addition in Figure 5.6 is the following:

- For complete precipitation of Mg^{2+}, 300 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 267 mg/L.
- A solid phase is generated: 175 mg/L of $Mg(OH)_2$.
- Final pH is 10.79.

The second survey is necessary to find the soda ash dosage for calcium precipitation (Figure 7.7).

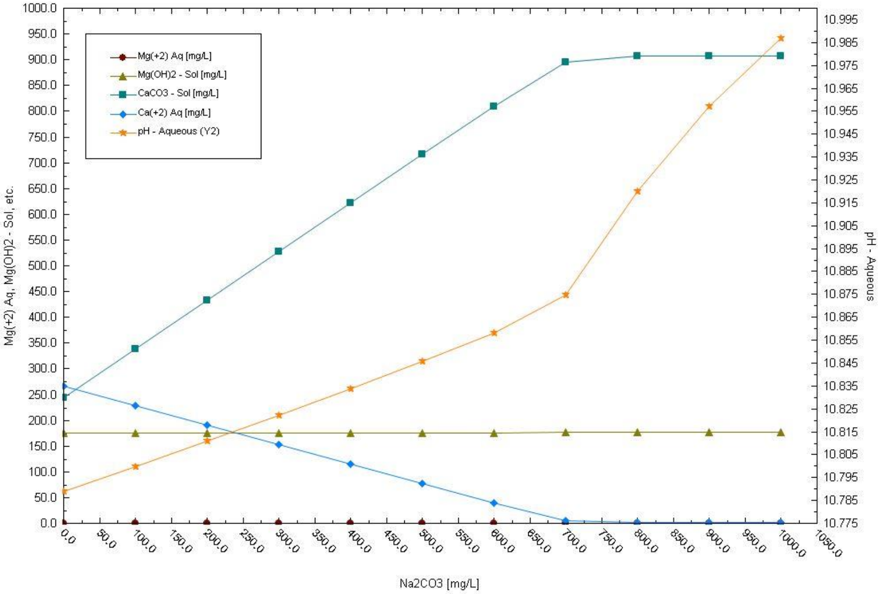


Figure 7.7 Plot obtained after "Survey" by composition of soda ash addition [OLI Analyzer Studio]

In Figure 7.7 the left and right ordinate axis represents the evolution of composition and pH respectively. In the abscissa axis the evolution of the addition of soda ash can be observed. This plot represents the continuation of the lime plot. The initial values of this graphic are the same of the final values of the lime graphic (Figure 7.6). Just in the moment to stop adding lime, it starts the soda ash addition. The magnesium hydroxide (olive line) remains constant and the magnesium (brown line) remains in zero because it had been removed in the lime-addition step. The calcium (blue line) is removed by the addition of soda ash and for this reason the calcium carbonate (green line) rises.

For Figure 7.7 the analysis is the following:

- For complete precipitation of Ca^{2+}, 700 mg/L of soda ash must be added.
- A solid phase is generated: 908 mg/L of $CaCO_3$.
- Final pH is 10.98.

8. RESULTS AND DISCUSSION

In this project there are two sets of simulations for different types of waters:

- Softening of water which characteristics have been obtained from scientific articles.
- Softening of water treated in the laboratory by adding chemicals in Jar Tests.

8.1. DATA OBTAINED FROM SCIENTIFIC ARTICLES

The simulations of natural and synthetic waters extracted from scientific articles have been done to achieve water without hardness to compare with the stoichiometric calculated values, and then comparing the OLI results with the obtained results by the authors (if reported). The objective was to reduce the hardness under 5 ppm of calcium and magnesium. It's known that is practically impossible to obtain a total removal of hardness for thermodynamic reasons (explained in section 5.1.1.), but the dosage of lime and soda ash to achieve these values can be determined by simulation with OLI. If the scientific article gives some results of calcium and magnesium removal, a comparison between these values and those obtained with OLI has also been done.

To do the stoichiometric calculations it must take into account the equation 5.49 to equation 5.54. In these reactions the stoichiometric relations can be seen.

To calculate the theoretical lime dose it is important to know that for each mole of lime added, a mole of magnesium can precipitate. For each mole of lime added, two mole of bicarbonate is transformed to carbonate and then one mole of carbonate react with one mole of calcium to precipitate as calcium carbonate. Therefore, the stoichiometric lime dose is the sum between the magnesium moles and the half of bicarbonate moles.

To calculate the theoretical soda ash dose it must be into account that it reacts with calcium one by one. The stoichiometric soda ash dose is the sum between natural dissolved calcium moles in water and the lime moles added (one mole of lime provides the water with one mole of calcium), minus the carbonic moles that react with lime in the first step.

8.1.1. SHEIKHOLESLAMI R. ET AL. [32]

First water composition is extracted from **Sheikholeslami R. et al.** [32]. The scientific article analyses well water pretreatment for feeding the water to a RO membrane process. The source water from well has the following reported analytical composition (Table 8.1).

Chemical specie	Concentration [mg/L]	Equivalent Weight	Concentration [meq/L]	Concentration [mg/L $CaCO_3$]
Ca^{2+}	176.2	20.0	8.8	440.5
Mg^{2+}	64.4	12.2	5.3	263.7
Na^{+}	58.4	23.0	2.5	127.0
Fe^{2+}	0.445	27.9	0.016	0.8
HCO_3^{-}	92.7	61.0	1.5	77.3
Cl^{-}	241.0	35.5	6.8	339.4
SO_4^{2-}	400.0	48.0	8.3	416.7
CO_2	9.0			
SiO_2	27.7			

Table 8.1 Data of water analysis from Sheikholeslami R. et al. [32]

Now, the bar diagram can be built (Figure 8.1).

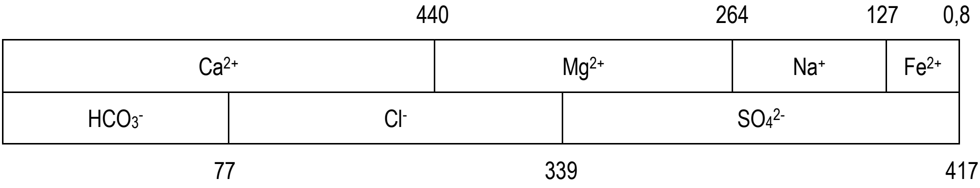


Figure 8.1 Bar diagram of feed water in mg/L as $CaCO_3$ (Self production)

The calcium concentration is bigger than the bicarbonate concentration, hence two steps is needed to reduce hardness in this water.

According to OLI, the feed water contains some calcium carbonate precipitated (137 mg/L). This precipitation is probably due to the water characteristics not known from the informed composition. Therefore, the amount of dissolved calcium in the stream created by OLI is 121 mg/L rather than the 176.19 reported in the article.

After the simulations with OLI two graphics of "Surveys" have been obtained (included in the Appendix, Figure A.1 and Figure A.2). For the first step (Figure A.1 and Table A.1 in the Appendix) the analysis is the following:

- For complete precipitation of Mg^{2+}, 250 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 243 mg/L.
- A solid phase is generated: 152 mg/L of $Mg(OH)_2$.
- Final pH is 10.71.

The lime consumption starts with the alkalization to precipitate calcium carbonate due to the CO_2 content. Lime reacts with CO_2 and HCO_3^- while raises the pH (eq. 5.49 and eq. 5.50). Then the magnesium starts to react with lime and to precipitate magnesium hydroxide until the amount of magnesium is under 1 ppm (eq. 5.52). Dissolved calcium rises for the calcium from the lime.

The second step is the addition of soda ash (Figure A.2 and Table A.2) gives:

- For complete precipitation of Ca^{2+}, 650 mg/L of soda ash must be added.
- A solid phase is generated: 769 mg/L of $CaCO_3$.
- Final pH is 10.81

As the author doesn't mention removal percentages, a stoichiometric analysis have been done. Using the equation 5.49 to equation 5.54 the theoretical dose of lime is 253 mg/L and the soda ash dose is 666 mg/L. The obtained results by OLI and by the stoichiometric calculations can be seen in Table 8.2.

Chemical specie	OLI	Stoichiometric Calculations
$CaOH_2$	250.0	253.0
Na_2CO_3	650.0	666.0

Table 8.2 Lime and Soda Ash dose obtained from OLI and from stoichiometric calculations

Finally, similar calcium and magnesium removal results obtained from OLI and from the stoichiometry can be observed. OLI make a good adjustment.

8.1.2. AL-REHAILI A. [33]

Al-Rehaili A. [33] gives the composition of two different waters: *Buwaib* and *Shemaisy*, two water treatment plants. The groundwater goes to a reverse osmosis (RO) process and it requires the reduction of calcium, magnesium and silica to safe levels in order to avoid the scale formation

8.1.2.1. BUWAIB

The source water from *Buwaib* has the following composition (Table 8.3).

Chemical specie	Concentration [mg/L]	Equivalent Weight	Concentration [meq/L]	Concentration [mg/L $CaCO_3$]
Ca^{2+}	202.0	20.0	10.1	505.0
Mg^{2+}	73.9	12.2	6.1	305.0
Fe^{2+}	0.21	27.9	0.0075	0.38
Na^{+}	325.7	23.0	14.2	708.0
Mn^{2+}	0.12	27.5	0.0044	0.22
HCO_3^-	150.0	61.0	2.5	122.9
Cl^-	380.0	35.5	10.7	535.2
SO_4^{2-}	732.0	48.0	15.3	762.5
NO_3^-	0.4	62.0	0.0065	0.32
F^-	1.12	19.0	0.059	2.9
SiO_2	34.6			

Table 8.3 Data of water analysis from Al-Rehaili A. [33] (*Buwaib*)

Now, the bar diagram can be built (Figure 8.2).

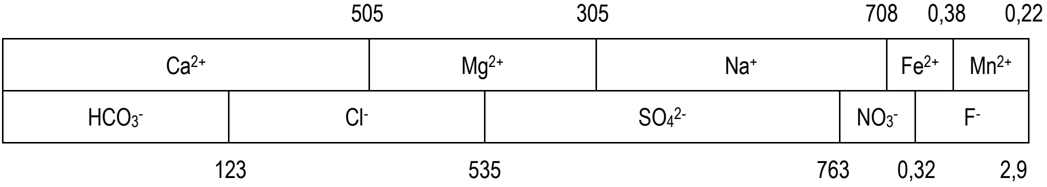


Figure 8.2 Bar diagram of feed water from Buwaib in mg/L as $CaCO_3$ (Self production)

The calcium concentration is bigger than the bicarbonate concentration, hence two steps is needed to reduce hardness in this water.

OLI reports some calcium carbonate precipitated (183 mg/L) probably due to the water characteristics not known from the informed composition. Therefore, the amount of dissolved calcium in the stream created by OLI is 128 mg/L rather than the 202 mg/L reported in the article.

After the simulations with OLI two graphics of “Surveys” have been obtained (Figure A.3 and Figure A.4). For the first step (Figure A.3 and Table A.3) the analysis is the following:

- For complete precipitation of Mg^{2+}, 300 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 267 mg/L.
- A solid phase is generated: 176 mg/L of $Mg(OH)_2$.
- Final pH is 10.79.

The second step (Figure A.4 and Table A.4) gives the following information:

- For complete precipitation of Ca^{2+}, 720 mg/L of soda ash must be added.
- A solid phase is generated: 902 mg/L of $CaCO_3$.
- Final pH is 10.88.

Now, a stoichiometric calculation has been done to see if the OLI results are on the right way. The stoichiometric lime dose is 316 mg/L and the theoretical soda ash dose is 726 mg/L. The obtained results by OLI and by the stoichiometric calculations can be seen in Table 8.4.

Chemical specie	OLI	Stoichiometric Calculations
$CaOH_2$	300.0	316.0
Na_2CO_3	700.0	726.0

Table 8.4 Lime and Soda Ash dose obtained from OLI and from stoichiometric calculations

In this case, the author gives some lime and soda ash dosages and a calcium and magnesium removal. Different simulations have been done with OLI to obtain results with the same lime and soda ash dose for comparison. The scientific article also gives the value of final pH; this is other point of comparison with the results reported from OLI.

The source water from *Buwaib* contains 202 mg/L of calcium and 73.9 mg/L of magnesium. The results obtained from OLI and from scientific article from *Buwaib* are given in Table 8.5.

Test	Input Dose		Al-Rehaili A. [33]			OLI		
	Lime Dose [mg/L]	Soda Ash Dose [mg/L]	Calcium Removed [%]	Magnesium Removed [%]	Final pH	Calcium Removed [%]	Magnesium Removed [%]	Final pH
1	90.0	260.0	56.4	5.7	9.23	72.4	21.0	9.81
2	90.0	300.0	64.0	11.3	9.34	79.7	21.1	9.81
3	110.0	260.0	31.2	13.8	9.63	67.1	29.7	9.83
4	110.0	300.0	32.5	16.1	9.53	74.5	29.8	9.83
5	110.0	340.0	31.2	4.7	9.05	81.8	29.9	9.83
6	130.0	300.0	62.7	5.7	9.65	69.3	38.4	9.86

Table 8.5 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Al-Rehaili A. [33] (*Buwaib*)

The initial pH of each simulation is the same in OLI and in the Jar Test reported by Al-Rehaili, and when the lime is added, the pH value rises.

From the analysis of results, OLI always gives higher calcium and magnesium removal than the scientific article. It could be assumed that the difference is due to an incomplete water description. This point also can be observed considering the final pH reached (see Table 8.5) The value of final pH in the Jar Test from scientific article is rather low. If this value is so low, the precipitation has not the optimum conditions and it won’t be so effective.

The results obtained in OLI regarding those reported in the scientific article can be seen graphically in Figure 8.3.

The similar results from OLI and from the stoichiometric calculations; and the low values of final pH given in the scientific article lead us to think that the water composition of the scientific article is incomplete.

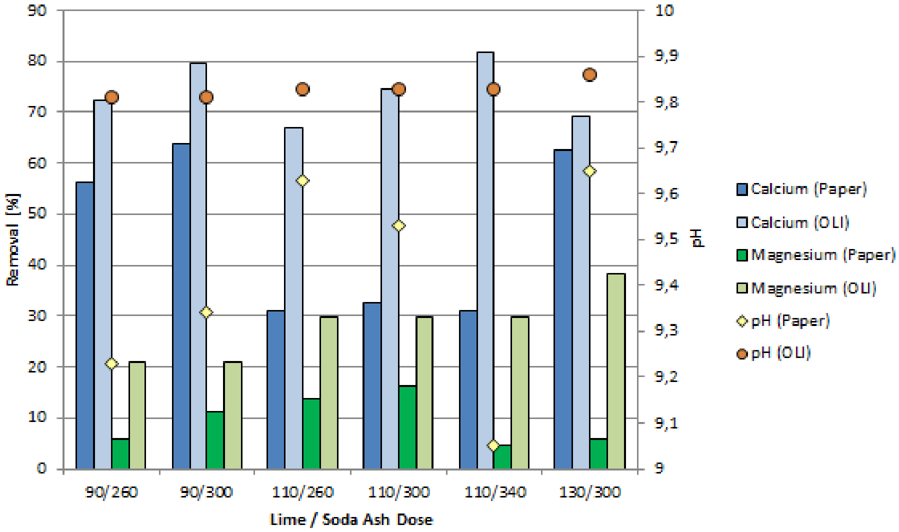


Figure 8.3 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Al-Rehaili A. [33] (*Buwaib*)

8.1.2.2. SHEMAISY

The source water from *Shemaisy* has the following composition (Table 8.6).

Chemical specie	Concentration [mg/L]	Equivalent Weight	Concentration [meq/L]	Concentration [mg/L $CaCO_3$]
Ca^{2+}	145.6	20.0	7.3	364.0
Mg^{2+}	39.1	12.2	3.2	160.3
Na^{+}	220.6	23.0	9.6	479.6
Fe^{2+}	0.36	27.9	0.013	0.65
Mn^{2+}	0.17	27.5	0.0062	0.31
HCO_3^{-}	180.0	61.0	2.9	147.5
Cl^{-}	171.0	35.5	4.8	240.8
SO_4^{2-}	498.0	48.0	10.4	518.8
NO_3^{-}	1.1	62.0	0.018	0.89
F^{-}	0.78	19.0	0.04	2.1
SiO_2	34.6			

Table 8.6 Data of water analysis from Al-Rehaili A. [33] (*Shemaisy*)

Now, the bar diagram can be built (Figure 8.4).

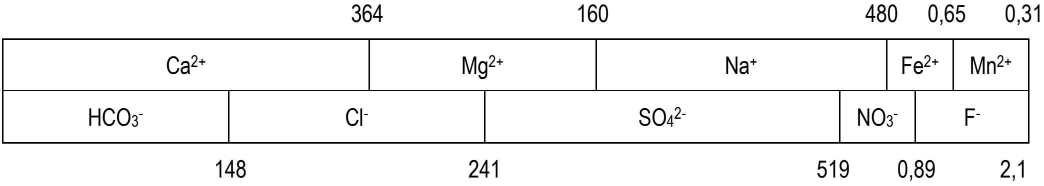


Figure 8.4 Bar diagram of feed water from Shemaisy in mg/L as $CaCO_3$ (Self production)

The calcium concentration is bigger than the bicarbonate concentration, hence two steps is needed to reduce hardness in this water.

After the simulations with OLI two graphics of “Surveys” have been obtained (Figure A.5 and Figure A.6). For the first step (Figure A.5 and Table A.5) the analysis is the following:

- For complete precipitation of Mg^{2+}, 200 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 136 mg/L.
- A solid phase is generated: 92 mg/L of $Mg(OH)_2$.
- Final pH is 10.78.

The second step (Figure A.6 Table A.6) gives the following information:

- For complete precipitation of Ca^{2+}, 380 mg/L of soda ash must be added.
- A solid phase is generated: 628 mg/L of $CaCO_3$.
- Final pH is 10.85.

Now, a stoichiometric calculation has been done. The stoichiometric lime dose is 228 mg/L and the theoretical soda ash dose is 399 mg/L. The obtained results by OLI and by the stoichiometric calculations can be seen in Table 8.4.

Chemical specie	**OLI**	**Stoichiometric Calculations**
$CaOH_2$	200.0	228.0
Na_2CO_3	380.0	399.0

Table 8.7 Lime and Soda Ash dose obtained from OLI and from stoichiometric calculations

In this case, the author also gives some lime and soda ash dosages and a calcium and magnesium removal. Different simulations have been done with OLI to obtain results with the same lime and soda ash dose for comparison.

The source water from *Shemaisy* contains 145.6 mg/L as calcium and 39.1 mg/L as magnesium. The results obtained from OLI and from scientific article from *Shemaisy* are given in Table 8.8.

	Input Dose		**Al-Rehaili A. [33]**			**OLI**		
	Lime Dose [mg/L]	**Soda Ash Dose [mg/L]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Final pH**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Final pH**
1	90.0	220.0	27.5	8.4	7.96	97.0	33.3	9.96
2	110.0	200.0	32.5	16.7	8.37	90.0	46.1	10.00
3	110.0	220.0	44.8	20.2	8.88	93.9	46.8	10.01
4	110.0	240.0	40.9	13.5	8.43	96.5	48.3	10.01
5	130.0	220.0	48.4	3.0	9.25	88.2	61.7	10.08

Table 8.8 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Al-Rehaili A. [33] (*Shemaisy*)

At same dose of chemicals, the removal is significantly higher with OLI. This situation is also reflected in the final pH reached in both cases. OLI predicts a higher final pH. Probably the water of scientific article is not well-defined.

The results can be seen molt clearly in Figure 8.5.

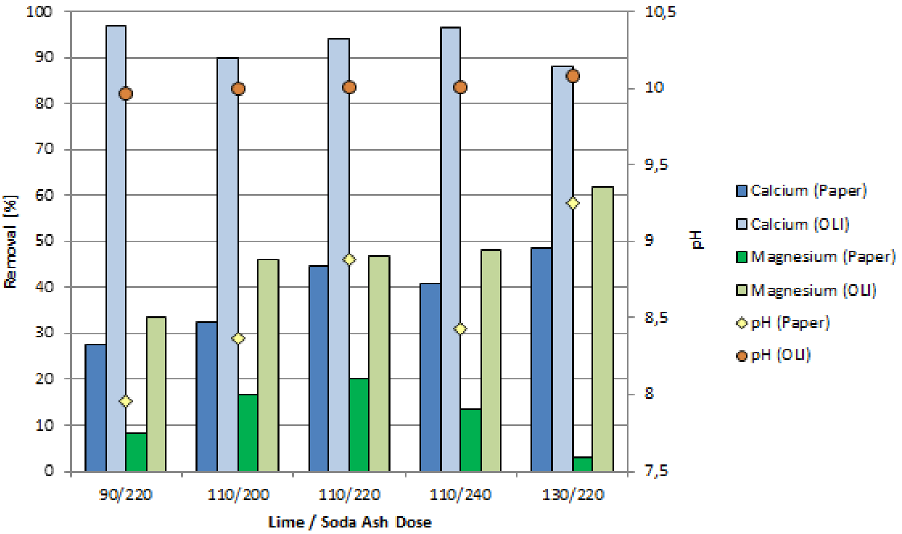


Figure 8.5 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Al-Rehaili A. [33] (*Shemaisy*)

8.1.3. CHEN S. ET AL. [34]

The next water composition is extracted from **Chen S. et al.** [34]. The scientific article studies the pretreatment to reduce the amount of calcium, magnesium and silica from brackish water. The softened water feeds a reverse osmosis process. The article is very interesting because it gives the removal percentage of calcium and magnesium for different doses of lime and soda ash (1:0, 1:3, 1:4). The source water has the following reported analytical composition (Table 8.9).

Chemical specie	Concentration [mg/L]	Equivalent Weight	Concentration [meq/L]	Concentration [mg/L $CaCO_3$]
Ca^{2+}	88.4	20.0	4.4	221.0
Mg^{2+}	81.3	12.2	6.7	333.2
HCO_3^-	135.0	61.0	2.2	110.7
Cl^-	1550.0	35.5	10.7	535.2
SiO_2	21.0			

Table 8.9 Data of water analysis from Chen S. et al. [34]

Now, the bar diagram can be built (Figure 8.6).

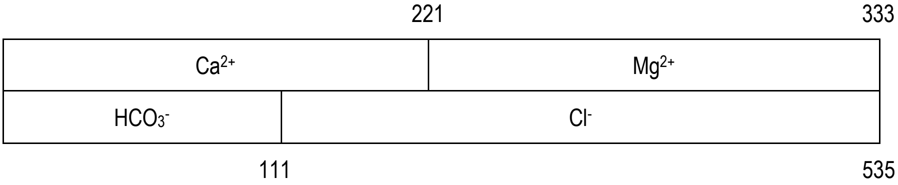


Figure 8.6 Bar diagram of feed brackish water in mg/L as $CaCO_3$ (Self production)

The calcium concentration is bigger than the bicarbonate concentration, hence two steps is needed to reduce hardness in this water.

After the simulations with OLI two graphics of “Surveys” have been obtained (Figure A.7 and Figure A.8). For the first step (Figure A.7 and Table A.7) the analysis is the following:

- For complete precipitation of Mg^{2+}, 345 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 187 mg/L.
- A solid phase is generated: 193 mg/L of $Mg(OH)_2$.
- Final pH is 10.75.

The second step is the addition of soda ash (Figure A.8 and Table A.8) which gives the following information:

- For complete precipitation of Ca^{2+}, 500 mg/L of soda ash must be added.
- A solid phase is generated: 676 mg/L of $CaCO_3$.
- Final pH is 10.80.

Now, a stoichiometric calculation has been done. The stoichiometric lime dose is 330 mg/L and the theoretical soda ash dose is 471 mg/L. The obtained results by OLI and by the stoichiometric calculations can be seen in Table 8.10.

Chemical specie	**OLI**	**Stoichiometric Calculations**
$CaOH_2$	345.0	330.0
Na_2CO_3	500.0	471.0

Table 8.10 Lime and Soda Ash dose obtained from OLI and from stoichiometric calculations

Now a comparison with the results from **Chen S. et al.** [34] will be done. The author gives different lime and soda ash dose ratios and the removal percentage of each dose. The results and comparison have been separated from each ratio to a better study.

The first ratio studied is 1:0. In this case there is a lime dose addition but there isn't a soda ash addition. The first lime added reacts with CO_2 and HCO_3^- while raises the pH and it removes a bit amount of calcium. Then the magnesium starts to react with lime and to precipitate in hydroxide magnesium form.

The source brackish water contains 88.4 mg/L of calcium and 81.3 mg/L of magnesium. The results obtained from OLI and from scientific article are given in Table 8.11.

	Input Dose		**Chen S. et al. [34]**		**OLI**		
	Lime Dose [mg/L]	**Soda Ash Dose [mg/L]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Final pH**
1	100.0	0.0	66.9	21.9	60.7	11.2	9.75
2	150.0	0.0	76.0	29.5	51.4	31.0	9.80
3	200.0	0.0	77.4	33.4	44.5	50.8	9.87
4	250.0	0.0	77.9	45.3	39.2	70.4	9.99
5	300.0	0.0	72.2	48.7	35.0	89.2	10.20

Table 8.11 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Chen S. et al. [34] (*Dose ratio 1:0*)

The results of calcium are quite low in OLI. In the values of Jar Test from article the calcium removed raises when the lime dose is bigger, but in OLI is the opposite, the calcium removal decreases when the lime dose rises. In the case of magnesium removed, it rise when the lime dose rises in the results from OLI and from article, but in the OLI results reach higher values of removal. All of this can be explained because OLI takes into account that the lime firstly react with CO_2 and HCO_3^- and removes some calcium, and then all the lime is to remove magnesium from water. On the other hand, the lime added in **Chen S. et al.** [34] reacts to remove calcium and magnesium. In Figure 8.7 the obtained results can be seen graphically.

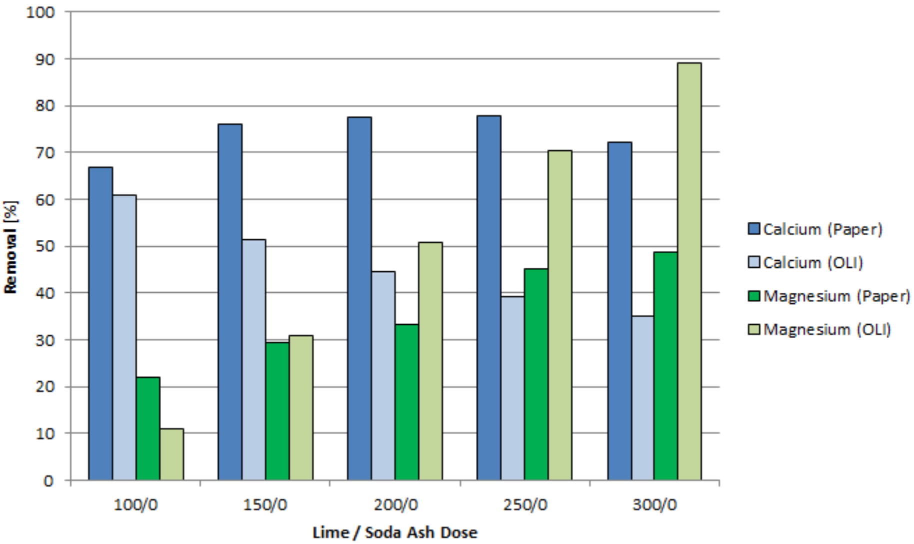


Figure 8.7 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Chen S. et al. [34] (Dose ratio 1:0)

The next analyzed ratio is 1:3. For each mg/L added of lime, three mg/L of soda ash will be added in the water to soften it. The results comparison can be seen in Table 8.12. The author does not inform the final pH reached.

	Input Dose		**Chen S. et al. [34]**		**OLI**		
	Lime Dose [mg/L]	**Soda Ash Dose [mg/L]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Final pH**
1	100.0	300.0	93.2	28.6	98.7	23.4	9.80
2	150.0	450.0	94.1	41.4	99.2	48.2	9.90
3	200.0	600.0	96.7	46.3	99.4	70.8	10.04
4	250.0	750.0	96.0	51.5	99.6	88.4	10.27
5	300.0	900.0	96.8	49.1	99.7	97.4	10.63

Table 8.12 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Chen S. et al. [34] (*Dose ratio 1:3*)

The results are similar than in the previous case. The calcium removed in OLI and in article in each simulation dose is very similar. The magnesium removed is similar when the soda ash dose is low, but when the dose is higher, the values are quite different. In Figure 8.8 the obtained results can be seen graphically.

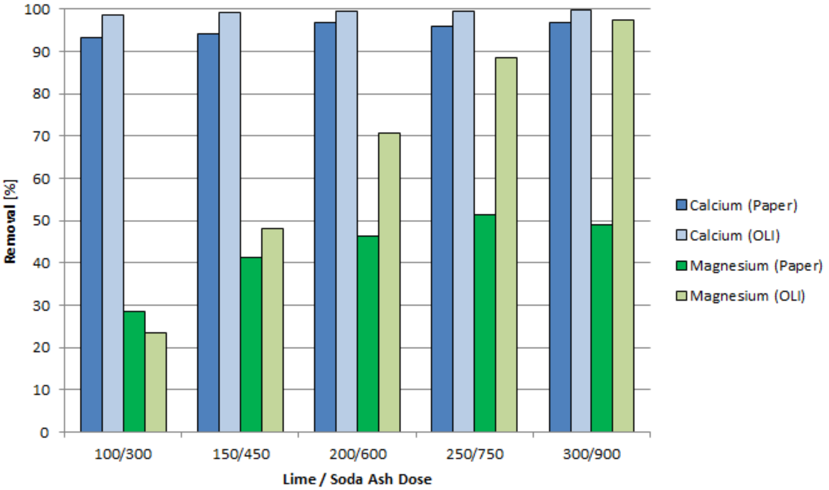


Figure 8.8 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Chen S. et al. [34] (*Dose ratio 1:3*)

The last analyzed ratio is 1:4. For each mg/L added of lime, four mg/L of soda ash will be added in the water to soften it. The results comparison can be seen in Table 8.13.

	Input Dose		**Chen S. et al. [34]**		**OLI**		
	Lime Dose [mg/L]	**Soda Ash Dose [mg/L]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Final pH**
1	100.0	400.0	91.0	21.1	99.0	30.7	9.84
2	150.0	600.0	92.8	36.8	99.4	57.5	9.97
3	200.0	800.0	95.2	44.2	99.5	79.2	10.15
4	250.0	1000.0	95.4	51.2	99.6	92.7	10.42
5	300.0	1200.0	95.2	46.1	99.7	98.2	10.75

Table 8.13 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Chen S. et al. [34] (*Dose ratio 1:4*)

In this case, the f calcium removal is also similar in the simulations with OLI and in the Jar Tests from article. The magnesium removals are different in each case. In Figure 8.9 the obtained results can be seen graphically.

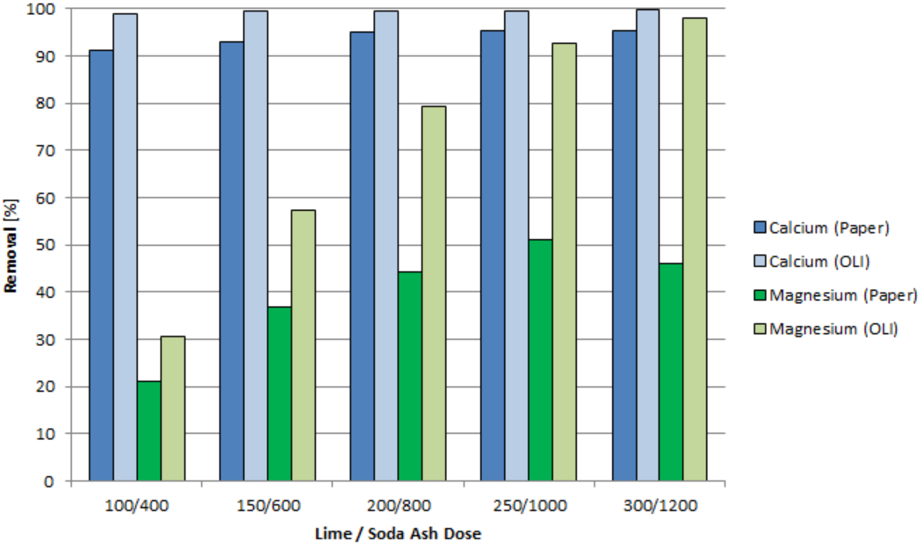


Figure 8.9 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Chen S. et al. [34] (*Dose ratio 1:4*)

When the process has two steps, lime and soda ash addition, the removal percentage of calcium in OLI and in article Jar Tests is very similar. But when the process only has one step (lime addition) the values of calcium removed are different. The magnesium removal percentage is similar with low amounts of lime added in all cases. Is probably that the water composition reported in the article is not complete, because also gives values of calcium, magnesium, bicarbonate and chloride, but this comparisons shows how OLI works.

8.1.4. MOHAMMADESMAEILI F. ET AL. [35]

The next two water compositions are extracted from **Mohammadesmaeili F. et al.** [35]. These two waters compositions are of two different plants. The first is from the city of *Goodyear* (Arizona) and the other is from the city of *Scottsdale* (Arizona). These plants have a reverse osmosis system to drinking water.

8.1.4.1. SCOTTSDALE

The source water from Scottsdale has the following composition (Table 8.14).

Chemical specie	Concentration [mg/L]	Equivalent Weight	Concentration [meq/L]	Concentration [mg/L $CaCO_3$]
Ca^{2+}	500.0	20.0	25.0	1250.0
Mg^{2+}	210.0	12.2	17.2	860.7
Na^{+}	1790.0	23.0	77.8	3891.3
K^{+}	260.0	39.1	6.7	332.5
HCO_3^{-}	850.0	61.0	13.9	696.7
Cl^{-}	2067.0	35.5	58.2	2911.3
SO_4^{2-}	2100.0	48.0	43.8	2187.5
NO_3^{-}	100.0	62.0	1.6	80.6
PO_4^{3-}	28.0	31.6	0.88	44.3
SiO_2	71.0			

Table 8.14 Data of water analysis from Mohammadesmaeili F. et al. [34] (*Scottsdale*)

Now, the bar diagram can be built (Figure 8.10).

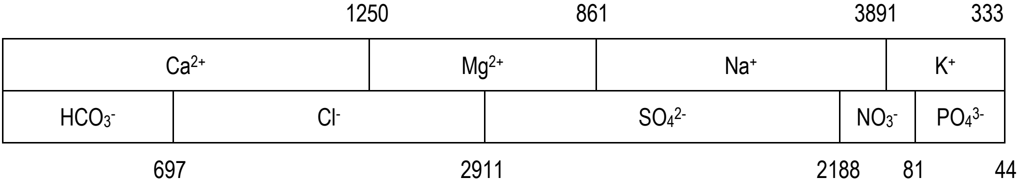


Figure 8.10 Bar diagram of feed water from Scottsdale in mg/L as $CaCO_3$ (Self production)

The calcium concentration is bigger than the bicarbonate concentration, hence two steps is needed to reduce hardness in this water.

For the first step (Figure A.9 and Table A.9) the analysis is the following:

- For complete precipitation of Mg^{2+}, 950 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 437 mg/L.
- A solid phase is generated: 503 mg/L of $Mg(OH)_2$.
- Final pH is 10.97.

The second step is the addition of soda ash (Figure A.10 and Table A.10) which gives the following information:

- For complete precipitation of Ca^{2+}, 1500 mg/L of soda ash must be added.
- A solid phase is generated: 2482 mg/L of $CaCO_3$.
- Final pH is 11.10.

It is important to take into account that in this simulation the calcium and magnesium amount is higher than the other simulations. The water hardness is high. For this reason the final pH of the water is higher than the other simulations.

Now, a stoichiometric calculation has been done. The stoichiometric lime dose is 1556 mg/L and the theoretical soda ash dose is 1500 mg/L. The obtained results by OLI and by the stoichiometric calculations can be seen in Table 8.15.

Chemical specie	OLI	Stoichiometric Calculations
$CaOH_2$	950.0	1156.0
Na_2CO_3	1500.0	1500.0

Table 8.15 Lime and Soda Ash dose obtained from OLI and from stoichiometric calculations

In this simulation, there are some differences in the results obtained with OLI and with stoichiometric calculations in the lime addition.

The author gives a lime and soda ash dose with a removal percentage and a simulation with OLI have done to compare the results.

The source water from *Scottsdale* contains 500 mg/L of calcium and 210 mg/L of magnesium. The results obtained from OLI and from scientific article from *Scottsdale* are given in Table 8.16.

Input Dose		**Mohammadesmaeili F. et al. [35]**		**OLI**		
Lime Dose [mg/L]	**Soda Ash Dose [mg/L]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Calcium Removed [%]**	**Magnesium Removed [%]**	**Final pH**
1500.0	2000.0	99.0	99.9	99.4	99.9	12.09

Table 8.16 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Mohammadesmaeili et al. [35] (*Scottsdale*)

The values of the comparison are selected to achieve a complete soft water. An almost free of calcium and magnesium water is obtained. The calcium and magnesium removal is the same in OLI simulations and in the values that article gives. It is not surprising these results given the very high doses of chemicals. The dose of chemicals in the article is higher than the necessary to reach the maximum removal of hardness (see doses from Table 8.15). This fact is supported by the final pH reached (12.09 as calculated by OLI).

In Figure 8.11 the obtained results can be seen graphically.

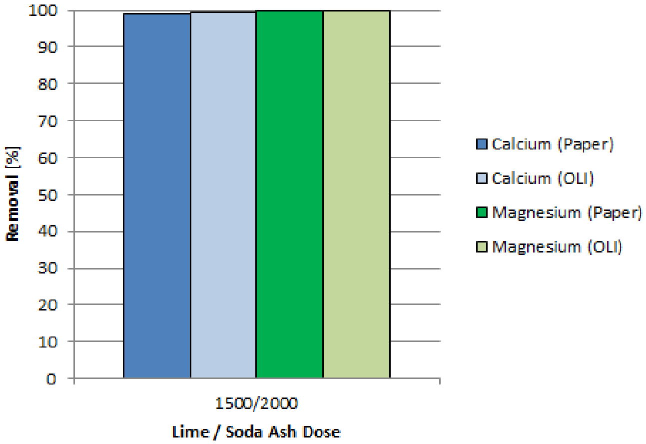


Figure 8.11 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Mohammadesmaeili. et al. [35] (*Scottsdale*)

8.1.4.2. GOODYEAR

The source water from Goodyear has the following composition (Table 8.17).

Chemical specie	Concentration [mg/L]	Equivalent Weight	Concentration [meq/L]	Concentration [mg/L $CaCO_3$]
Ca^{2+}	550.0	20.0	27.5	1375.0
Mg^{2+}	310.0	12.2	25.4	1270.5
Na^+	1373.0	23.0	59.7	2984.8
K^+	20.0	39.1	0.51	25.6
HCO_3^-	650.0	61.0	10.7	532.8
Cl^-	1950.0	35.5	54.9	2746.5
SO_4^{2-}	1650.0	48.0	34.4	1718.8
NO_3^-	210.0	62.0	3.4	169.4
PO_4^{3-}	4.0	31.6	0.13	6.3
SiO_2	63.0			

Table 8.17 Data of water analysis from Mohammadesmaeili F. et al. [35] (*Goodyear*)

Now, the bar diagram can be built (Figure 8.12).

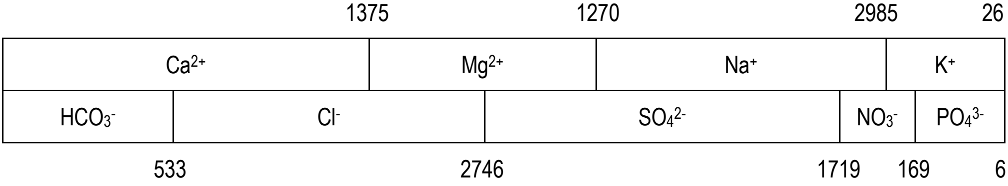


Figure 8.12 Bar diagram of feed water from Goodyear in mg/L as $CaCO_3$ (Self production)

For the first step (Figure A.11 and Table A.11) the analysis is the following:

- For complete precipitation of Mg^{2+}, 1100 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 716 mg/L.
- A solid phase is generated: 743 mg/L of $Mg(OH)_2$.
- Final pH is 11.11.

The second step is the addition of soda ash (Figure A.12 and Table A.12) which gives the following information:

- For complete precipitation of Ca^{2+}, 2250 mg/L of soda ash must be added.
- A solid phase is generated: 2853 mg/L of $CaCO_3$.
- Final pH is 11.25.

Now, a stoichiometric calculation has been done. The stoichiometric lime dose is 1340 mg/L and the theoretical soda ash dose is 2242 mg/L. The obtained results by OLI and by the stoichiometric calculations can be seen in Table 8.18.

Chemical specie	OLI	Stoichiometric Calculations
$CaOH_2$	1100.0	1340.0
Na_2CO_3	2250.0	2242.0

Table 8.18 Lime and Soda Ash dose obtained from OLI and from stoichiometric calculations

The source water from Scottsdale contains 550 mg/L of calcium and 310 mg/L of magnesium. The results comparison from Goodyear is given in Table 8.19.

	Input Dose		Mohammadesmaeili F. et al. [35]		OLI		
	Lime Dose [mg/L]	Soda Ash Dose [mg/L]	Calcium Removed [%]	Magnesium Removed [%]	Calcium Removed [%]	Magnesium Removed [%]	Final pH
1	1350.0	1860.0	52.7	96.8	73.0	99.9	11.82

Table 8.19 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Mohammadesmaeili et al. [35] (*Goodyear*)

The dose in the water from Goodyear achieves almost free magnesium water (in OLI simulations and in Jar Test results from article). The soda ash dose is not enough for the total calcium removal. The percentage of calcium removed is bit different in OLI and in the values that the article gives. In Figure 6.13 the obtained results can be seen graphically.

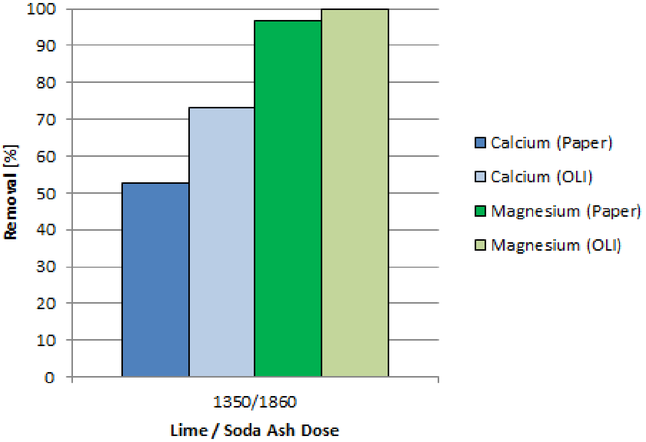


Figure 8.13 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from Mohammadesmaeili. et al. [35] (*Goodyear*)

8.2. DATA OBTAINED FROM LABORATORY JAR TESTS

In this section seven waters have been simulated. The Table 8.20 summarizes their characteristics. All samples have been selected because they were previously softened by chemical precipitation in the laboratory. The first water is an industrial process water. The aim of the treatment is to use the water as feed for a membrane treatment. Thus, it has been treated with lime and soda ash to remove calcium and magnesium. The other six waters are synthetic waters that were prepared in the laboratory for softening with caustic soda and/or sodium carbonate by Jar Tests.

The synthetic waters contains calcium and/or magnesium and silica. The ions were added in form of calcium chloride ($CaCl_2$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and sodium metasilicate (Na_2SiO_3). The pH adjustment of the synthetic waters has been done with hydrochloric acid (HCl). There are six simulations of six synthetic waters with different calcium, magnesium and silica concentrations, but the six waters have the same initial pH of 7. These waters have been treated with sodium hydroxide (NaOH) to remove calcium and magnesium. The caustic soda softening (explained in section 5.1.2.) is very similar to the lime softening. The advantage is that caustic soda do not increase dissolved calcium in the water while it is been treated. Therefore, less amount of soda ash is needed. The disadvantage is that the caustic softening is more expensive than the lime process.

Simulation	Water type	Main Ion
1	Industrial	Ca, Mg, Si
2	Synthetic 1	Mg, Si
3	Synthetic 2	Mg, Si
4	Synthetic 3	Mg, Ca, Si
5	Synthetic 4	Mg, Ca, Si
6	Synthetic 5	Ca, Si
7	Synthetic 6	Ca, Si

Table 8.20 Summary of the type of water simulated

Different calcium and magnesium concentration can be seen in each synthetic water (Table 8.20). The first two water simulations don’t have calcium, in these cases, only one step is needed, the sodium hydroxide addition. This caustic soda raises the pH and the magnesium precipitates in magnesium hydroxide form. In these cases no soda ash is added because there isn't calcium in the water and the first step is done with caustic soda and calcium is not added. The water simulation three, four and five have calcium and magnesium. Therefore, two steps are needed to remove hardness, a caustic soda softening to remove magnesium and a soda ash addition to remove calcium. The last water simulations contains calcium but it doesn't contain magnesium, in this case, the process only have one step, the addition of soda ash to remove the calcium.

8.2.1. SIMULATION 1: INDUSTRIAL WATER

The water composition of the first simulation has been extracted from its analytical data. This water feeds a reverse osmosis process. Calcium and magnesium removal are available to compare the results obtained with OLI. Two strategies have been simulated, the complete calcium and magnesium removal (under 5 ppm) and the removal until 150 ppm of calcium and 20 ppm of magnesium. This water has de following composition (Table 8.21).

Chemical specie	Concentration [mg/L]	Equivalent Weight	Concentration [meq/L]	Concentration [mg/L $CaCO_3$]
Ca^{2+}	328.0	20.0	16.4	820.0
Mg^{2+}	112.0	12.2	9.18	459.0
Na^{+}	2322.0	23.0	100.9	5047.8
K^{+}	246.0	39.1	6.3	314.6
HCO_3^-	386.0	61.0	6.3	316.4
Cl^-	2943.0	35.5	82.9	4145.1
SO_4^{2-}	1525.0	48.0	31.8	1588.5
NO_3^-	64.0	62.0	1.0	51.6
F^-	3.0	31.6	0.09	4.8
SiO_2	112.0			

Table 8.21 Data of water analysis from industrial water

Now, the bar diagram can be built (Figure 8.14).

Figure 8.14 Bar diagram of feed water in mg/L as $CaCO_3$ (Self production)

The calcium concentration is bigger than the bicarbonate concentration, hence two steps is needed to reduce hardness in this water.

Firstly, the simulation for complete calcium and magnesium removal has been done. After the simulations with OLI two graphics of “Surveys” have been obtained (See Appendix, Figure A.13 and Figure A.14). For the first treatment step (Appendix Figure A.13 and Table A.13) the resulting analysis is the following:

- For complete precipitation of Mg^{2+}, 600 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 399 mg/L.
- A solid phase is generated: 258 mg/L of $Mg(OH)_2$.
- Final pH is 10.5.

The second step is the addition of soda ash (Figure A.14 and Table A.14) which gives the following information:

- For almost complete precipitation of Ca^{2+}, 1100 mg/L of soda ash must be added.
- A solid phase is generated: 1621 mg/L of $CaCO_3$.
- Final pH is 10.54.

Now, a stoichiometric calculation has been done. For comparison, the results by OLI, by the stoichiometric calculations, and by Jar Test at laboratory are shown in Table 8.22.

Chemical specie	OLI	Stoichiometric Calculations	Jar Test
$CaOH_2$	600	576	672
Na_2CO_3	1100	1021	1115

Table 8.22 Lime and Soda Ash doses obtained from OLI, stoichiometry, and Jar Test

In both, OLI and Jar test at laboratory, the final dissolved calcium and magnesium reached was approximately 5 ppm. As can be observed from table 8.22 the results are very similar in all cases. Respect to the laboratory doses, the OLI calculated values are 10% lower for lime and 1% lower for soda ash. The removal obtained by stoichiometric calculations is between 8% (for soda ash) and 14% (for lime) lower. The difference for the jar test doses can be explained considering the complexity of the matrix of the real water that may demand more concentration of chemicals to perform the precipitation.

The second simulation to obtain a partial removal of calcium and magnesium has been done. In real cases some residuals of dissolved calcium and magnesium are accepted (i.e. RO membranes using antiscaling). In this simulation case, the calcium and magnesium removal is extended up to 150 mg/L of calcium and 20 mg/L of magnesium. After the simulations with OLI two graphics of “Surveys” have been obtained (Figure A.15 and Figure A.16). For the first step (Figure A.15 and Table A.15) the analysis is the following:

- Until 20 ppm of Mg^{2+}, 540 mg/L of lime must be added.
- Dissolved Ca^{2+} at the end of the Mg^{2+} precipitation is 367 mg/L.
- A solid phase is generated: 220 mg/L of $Mg(OH)_2$.
- Final pH is 10.11.

The second step is the addition of soda ash (Figure A.16 and Table A.16) which gives the following information:

- Until 150 ppm of Ca^{2+}, 580 mg/L of soda ash must be added.
- A solid phase is generated: 1178 mg/L of $CaCO_3$.
- Final pH is 10.11.

In this simulation the final pH is low allowing a partial calcium and magnesium removal.

For comparison, the results by OLI and by the Jar test at laboratory are shown in Table 8.23.

Chemical specie	OLI	Jar Test
$CaOH_2$	540	565
Na_2CO_3	580	623

Table 8.23 Lime and Soda Ash dose obtained from OLI and from lab results

Comparing the results, OLI calculates a dose of lime of 4% lower than the necessary for the laboratory test. For soda ash, OLI calculates a dose 7% lower. The results are very similar.

8.2.2. SIMULATION 2: SYNTHETIC WATER 1

The synthetic water 1 has the following composition (Table 8.24.).

Simulation	$CaCl_2$ [mg/L]	$MgCl_2·6H_2O$ [mg/L]	Na_2SiO_3 [mg/L]	HCl [mg/L]
2	0.0	655.6	179.8	107.3

Table 8.24 Data of water analysis from synthetic water 1

Calcium, magnesium, and silica concentrations of synthetic water 1 are in Table 8.25.

Simulation	Ca^+ [mg/L]	Mg^{2+} [mg/L]	SiO_2 [mg/L]
2	0.0	78.4	88.5

Table 8.25 Data of water composition from synthetic water 1

The sodium hydroxide and soda ash dose used in simulation 2 can be seen in Table 8.26.

Simulation	NaOH [mg/L]	Na_2CO_3 [mg/L]
2	420.0	0.0

Table 8.26 Used dose in simulation 2

The simulation 2 (Figure A.17 and Table A.17) only has one step of caustic soda addition and the analysis is the following.

- All dissolved magnesium is removed.
- A solid phase is generated: 188 mg/L of $Mg(OH)_2$.
- Final pH is 11.36.

8.2.3. SIMULATION 3: SYNTHETIC WATER 2

The synthetic water 2 has the following composition (Table 8.27.).

Simulation	$CaCl_2$ [mg/L]	$MgCl_2·6H_2O$ [mg/L]	Na_2SiO_3 [mg/L]	HCl [mg/L]
3	0.0	380.6	175.9	104.9

Table 8.27 Data of water analysis from synthetic water 2

Calcium, magnesium, and silica concentrations of synthetic water 2 are in Table 8.28.

Simulation	Ca^+ [mg/L]	Mg^{2+} [mg/L]	SiO_2 [mg/L]
3	0.0	45.5	86.6

Table 8.28 Data of water composition from synthetic water 2

The sodium hydroxide and soda ash dose used in simulation 2 can be seen in Table 8.29.

Simulation	NaOH [mg/L]	Na_2CO_3 [mg/L]
3	255.0	0.0

Table 8.29 Used dose in simulation 3

The simulation 3 (Figure A.18 and Table A.18) only has one step of caustic soda addition and the analysis is the following.

- All dissolved magnesium is removed.
- A solid phase is generated: 108 mg/L of $Mg(OH)_2$.
- Final pH is 11.05.

8.2.4. SIMULATION 4: SYNTHETIC WATER 3

The synthetic water 3 has the following composition (Table 8.30.).

Simulation	$CaCl_2$ [mg/L]	$MgCl_2·6H_2O$ [mg/L]	Na_2SiO_3 [mg/L]	HCl [mg/L]
4	121.0	354.4	205.5	122.6

Table 8.30 Data of water analysis from synthetic water 3

Calcium, magnesium, and silica concentrations of synthetic water 3 are in Table 8.31.

Simulation	Ca^+ [mg/L]	Mg^{2+} [mg/L]	SiO_2 [mg/L]
4	43.8	42.4	101.2

Table 8.31 Data of water composition from synthetic water 3

The sodium hydroxide and soda ash dose used in simulation 4 can be seen in Table 8.32.

Simulation	NaOH [mg/L]	Na_2CO_3 [mg/L]
4	270.0	318.0

Table 8.32 Used dose in simulation 4

For the first step in the simulation 4 (Figure A.19 and Table A.19) the analysis is the following.

- All dissolved magnesium is removed.
- A solid phase is generated: 100 mg/L of $Mg(OH)_2$.
- Final pH is 11.10.

The second step in the simulation 4 (Figure A.20 and Table A.20) gives the following information.

- All dissolved calcium is removed.
- A solid phase is generated: 107 mg/L of $CaCO_3$.
- Final pH is 11.19.

8.2.5. SIMULATION 5: SYNTHETIC WATER 4

The synthetic water 4 has the following composition (Table 8.33.).

Simulation	$CaCl_2$ [mg/L]	$MgCl_2 \cdot 6H_2O$ [mg/L]	Na_2SiO_3 [mg/L]	HCl [mg/L]
5	247.6	358.3	192.0	114.6

Table 8.33 Data of water analysis from synthetic water 4

Calcium, magnesium, and silica concentrations of synthetic water 4 are in Table 8.34.

Simulation	Ca^+ [mg/L]	Mg^{2+} [mg/L]	SiO_2 [mg/L]
5	89.4	42.8	94.5

Table 8.34 Data of water composition from synthetic water 4

The sodium hydroxide and soda ash dose used in simulation 5 can be seen in Table 8.35.

Simulation	NaOH [mg/L]	Na_2CO_3 [mg/L]
5	270.0	530.0

Table 8.35 Used dose in simulation 5

For the first step in the simulation 5 (Figure A.21 and Table A.21) the analysis is the following.

- All dissolved magnesium is removed.
- A solid phase is generated: 102 mg/L of $Mg(OH)_2$.
- Final pH is 11.07.

The second step in the simulation 5 (Figure A.22 and Table A.22) gives the following information.

- All dissolved calcium is removed.
- A solid phase is generated: 221 mg/L of $CaCO_3$.
- Final pH is 11.21.

8.2.6. SIMULATION 6: SYNTHETIC WATER 5

The synthetic water 5 has the following composition (Table 8.36.).

Simulation	**$CaCl_2$ [mg/L]**	**$MgCl_2 \cdot 6H_2O$ [mg/L]**	**Na_2SiO_3 [mg/L]**	**HCl [mg/L]**
6	267.5	383.3	207.2	123.7

Table 8.36 Data of water analysis from synthetic water 5

Calcium, magnesium, and silica concentrations of synthetic water 5 are in Table 8.37.

Simulation	**Ca^+ [mg/L]**	**Mg^{2+} [mg/L]**	**SiO_2 [mg/L]**
6	132.7	45.8	102.0

Table 8.37 Data of water composition from synthetic water 5

The sodium hydroxide and soda ash dose used in simulation 6 can be seen in Table 8.38

Simulation	**NaOH [mg/L]**	**Na_2CO_3 [mg/L]**
6	270.0	740.0

Table 8.38 Used dose in simulation 6

For the first step in the simulation 6 (Figure A.23 and Table A.23) the analysis is the following.

- All dissolved magnesium is removed.
- A solid phase is generated: 109 mg/L of $Mg(OH)_2$.
- Final pH is 10.92.

The second step in the simulation 6 (Figure A.24 and Table A.24) gives the following information.

- All dissolved calcium is removed.
- A solid phase is generated: 329 mg/L of $CaCO_3$.
- Final pH is 11.14.

8.2.7. SIMULATION 7: SYNTHETIC WATER 6

The synthetic water 6 has the following composition (Table 8.39.).

Simulation	**$CaCl_2$ [mg/L]**	**$MgCl_2 \cdot 6H_2O$ [mg/L]**	**Na_2SiO_3 [mg/L]**	**HCl [mg/L]**
7	260.4	0.0	207.4	123.8

Table 8.39 Data of water analysis from synthetic water 6

Calcium, magnesium, and silica concentrations of synthetic water 6 are in Table 8.40.

Simulation	**Ca^+ [mg/L]**	**Mg^{2+} [mg/L]**	**SiO_2 [mg/L]**
7	94.0	0.0	102.1

Table 8.40 Data of water composition from synthetic water 6

The sodium hydroxide and soda ash dose used in simulation 7 can be seen in Table 8.41

Simulation	**NaOH [mg/L]**	**Na_2CO_3 [mg/L]**
7	0.0	530.0

Table 8.41 Used dose in simulation 7

The last simulation (Figure A.25 and Table A.25) only has one step of soda ash addition and the analysis is the following.

- All dissolved calcium is removed.
- A solid phase is generated: 232 mg/L of $CaCO_3$.
- Final pH is 10.06.

8.2.8. COMBINED RESULTS FROM SYNTHETIC WATERS

In each simulation by OLI the final pH can be seen. The pH reached depends on the species to precipitate.

Now, the removals of dissolved calcium and magnesium from laboratory Jar Tests and from the OLI calculations are shown in Table 8.42. It must be taking into account that the doses of chemicals depend on the initial concentration of Mg^{2+} and/or Ca^{2+}.

Test	Input Dose		Laboratory Jar Tests		OLI		
	Caustic Soda Dose [mg/L]	Soda Ash Dose [mg/L]	Calcium Removed [%]	Magnesium Removed [%]	Calcium Removed [%]	Magnesium Removed [%]	Final pH
2	420.0	0.0	0.0	93.7	0.0	99.8	11.36
3	255.0	0.0	0.0	84.8	0.0	99.1	11.05
4	270.0	318.0	83.0	80.5	97.8	99.2	11.19
5	270.0	530.0	90.8	84.6	98.9	99.2	11.21
6	270.0	740.0	97.1	85.5	99.3	98.7	11.14
7	0.0	530.0	93.9	0.0	98.9	0.0	10.06

Table 8.42 Removal of Ca^{2+} and Mg^{2+} obtained from OLI and from laboratory Jar Tests

The removals of calcium are similar in laboratory Jar Tests and in OLI. Even though, the results of calcium removal are slightly higher in OLI than the Jar Tests (the average deviation is 8%).

The magnesium removal is very high in both cases, but the removal of magnesium is higher in OLI in all cases (the maximum difference is the 19% given by simulation 4, the average is 13% of deviation). These results can be seen graphically in Figure 8.15 and 8.16.

The lower removal obtained by real chemical precipitation can be explained by thermodynamic (explained in section 5.1.1.). In OLI a completely calcium and magnesium removal is achieved.

In such cases a safety factor can be introduced to equalize the results and to improve its calculations and enhance the ability to predict the behavior of the physic-chemical treatment.

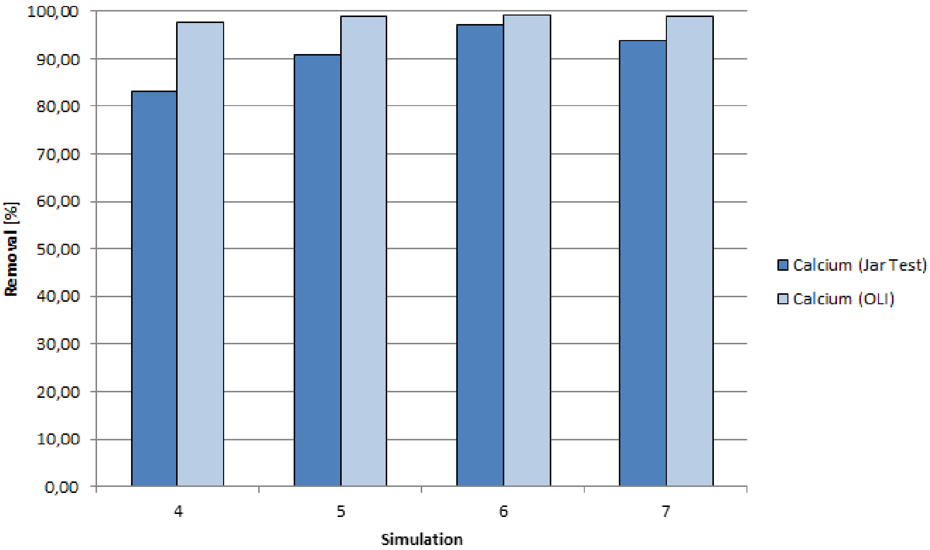


Figure 8.15 Removal of Ca^{2+} obtained from OLI and from laboratory Jar Tests

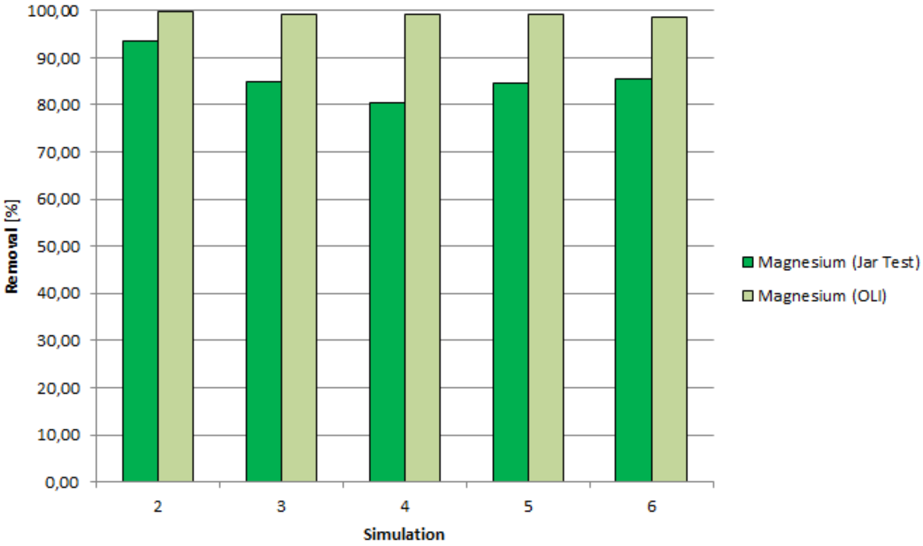


Figure 8.16 Removal of Mg^{2+} obtained from OLI and from laboratory Jar Tests

9. CONCLUSIONS

Nowadays, chemical precipitation is one of the most used and effective softening processes. Lime soda ash softening is one of the most feasible methods for the removal of dissolved calcium and magnesium from water. This fact has been studied by the analysis of all water softening processes.

This process has some advantages, for example, the chemicals are not expensive and it is a simple process. Lime and soda ash softening removes dissolved calcium and magnesium in the water stream and it also reduces the amount of some others substances as silica and heavy metals such as iron or manganese. On the other hand, this process produces a constantly sludge stream. These sludge streams must be treated.

The caustic soda softening process is very similar to the lime softening. The caustic soda softening is more efficient than the other due to sodium hydroxide is a strong base and it raises the pH with less amount of product. Moreover, the soda ash amount used to remove calcium caustic soda softening is lower than the soda ash used in lime and soda ash softening, because sodium hydroxide does not provides the water with more calcium as lime. However, the caustic soda is more expensive than lime. Thus, the lime and soda ash softening is more economical than caustic soda and soda ash softening.

After many simulations with OLI, the removals of calcium and magnesium are similar in the OLI simulations and in the laboratory Jar Tests. OLI describes treatment process in an automated manner through a series of internal data; hence it is very important to define perfectly the composition of the analyzed water stream. OLI works with a database and it simulates specific situations using thermodynamics. If the analyzed water is not well-defined, OLI will not be able to assume certain chemical interactions that will occur in the reality.

In the case of water composition and treatment extracted from scientific articles, not always a good agreement by OLI calculations is reached. This behavior is probably due to fact that in scientific articles the water composition information is not complete and gives different final removals. This point is supported by the differences found in final pH reported. Also the stoichiometric calculations performed to compare with OLI results give a good agreement.

In the cases in which the simulations are done from laboratory data (lime/sodium hydroxide and soda ash softening) the results in OLI simulations and in the laboratory Jar Tests have a good adjustment. Here again, stoichiometric calculations also agreed with OLI calculations.

There are cases in which a safety factor can be applied in order to equalize the OLI results to the real chemical treatment. A deeper analysis must be done to establish the appropriate correlation.

OLI presents an additional advantage if the water to be treated is not yet available (in treatment process design). In cases with poorly defined stream water composition, to perform OLI simulations before the laboratory Jar Tests are very advisable. These simulations give an initial idea of the amount of chemicals necessary to obtain a specific water quality for its final use.

After many simulations, it would be suitable to say that OLI is a very useful tool to reduce time and costs invested in the laboratory. OLI allows us to obtain a similar removal results that those obtained in the laboratory. OLI is an easy-to-use and powerful software that can perform many interesting operations.

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12. ACRONYMS

AQ – Aqueous Model

MSE – Mixed Solvent Electrolyte Model

RO – Reverse Osmosis

UNIFAC – Universal Functional-group Activity Coefficients Model

APPENDICES

APPENDIX 1. GRAPHICS AND TABLES FROM OLI

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.1153e5	1.11539e5	5.27073
Na(+1)	95.3583	95.3705	0.0
Ca(+2)	311.41	243.198	68.252
Fe(+2)	0.444978	0.0206597	0.424374
Mg(+2)	64.3468	0.993609	63.3613
O(-2)	8.85568e5	8.85515e5	165.402
Cl(-1)	240.988	241.019	0.0
C(+4)	20.707	0.254893	20.4547
S(+6)	133.513	133.53	0.0
Si(+4)	12.7603	12.762	0.0

Table A.1 Water oncentrations after first step for softening, lime addition (Self production)

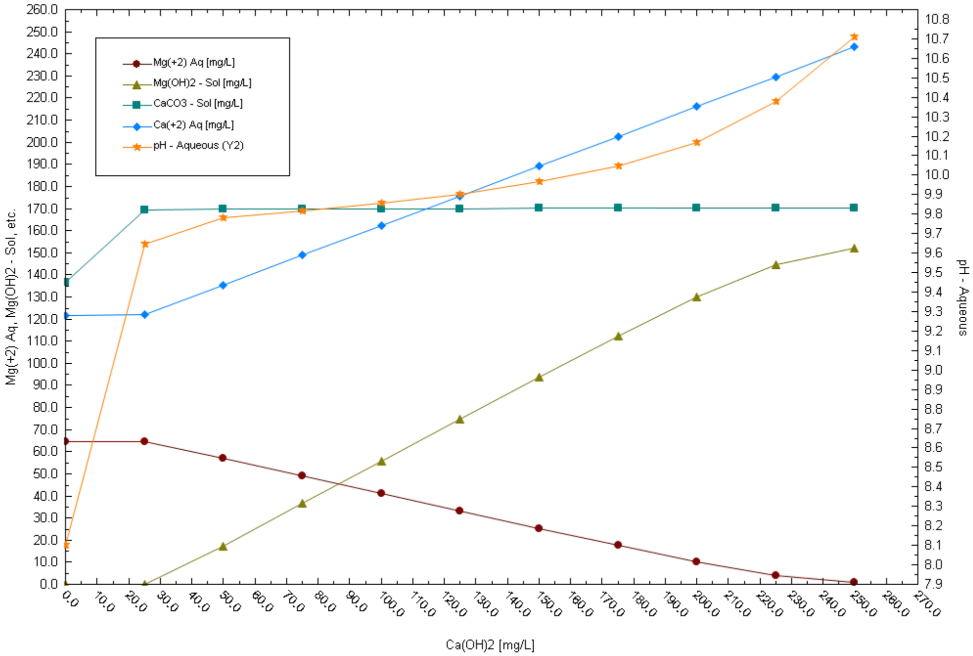


Figure A.1 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11498e5	1.11531e5	5.30211
Na(+1)	377.339	377.471	0.0
Ca(+2)	311.41	3.47043	308.048
Fe(+2)	0.444978	0.0200317	0.425101
Mg(+2)	64.3468	0.629817	63.7394
O(-2)	8.85603e5	8.85459e5	453.084
Cl(-1)	240.988	241.072	0.0
C(+4)	94.3676	2.08029	92.3202
S(+6)	133.513	133.56	0.0
Si(+4)	12.7603	12.7648	0.0

Table A.2 Water concentrations after second step for softening, soda ash addition (Self production)

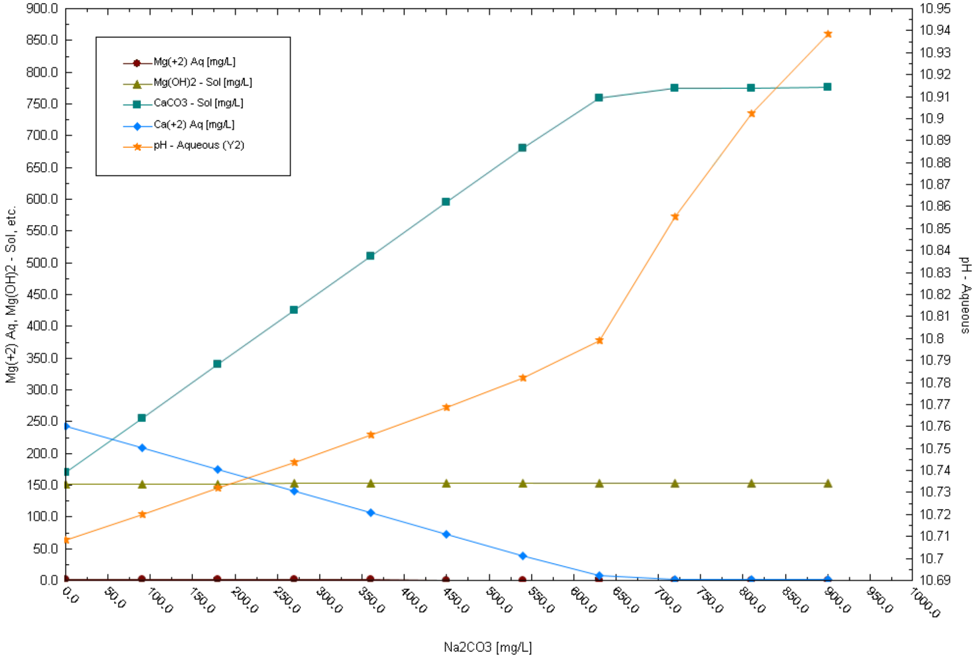


Figure A.2 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11515e5	1.11528e5	6.07356
Na(+1)	325.733	325.786	0.0
Ca(+2)	364.261	266.648	97.673
Fe(+2)	0.209986	0.0185211	0.191499
Mg(+2)	73.915	0.78521	73.1419
Mn(+2)	0.119992	0.120012	0.0
F(-1)	1.11992	1.12011	0.0
O(-2)	8.8572e5	8.85652e5	213.38
Cl(-1)	379.974	380.037	0.0
C(+4)	29.5252	0.258052	29.272
S(+6)	244.325	244.365	0.0
N(+5)	0.0903527	0.0903675	0.0
Si(+4)	16.1722	16.1748	0.0

Table A.3 Water concentrations after first step for softening, lime addition (Self production)

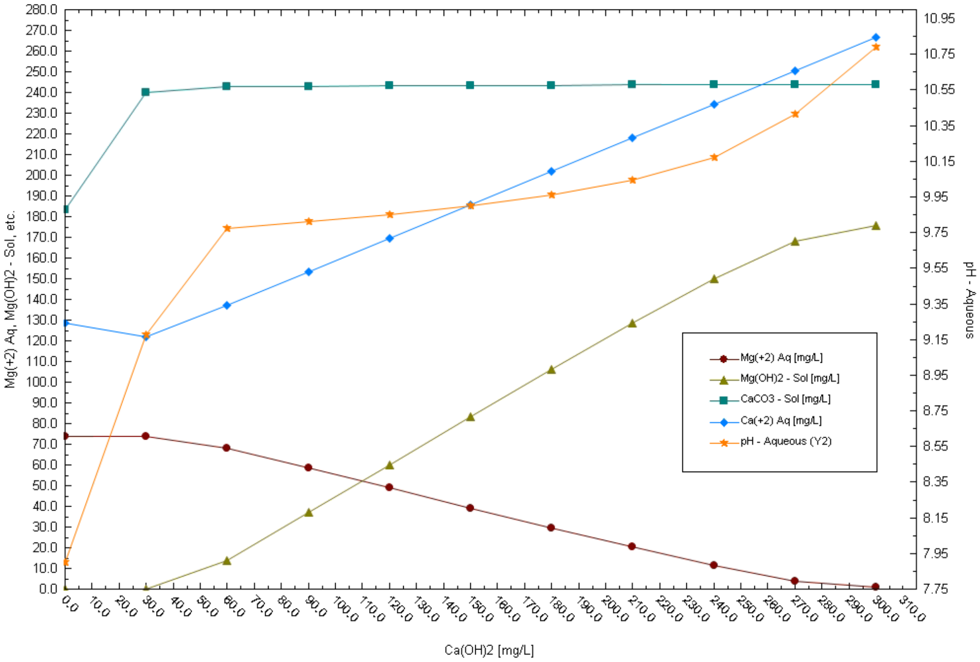


Figure A.3 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.1148e5	1.11519e5	6.09714
Na(+1)	638.081	638.341	0.0
Ca(+2)	364.261	3.19796	361.212
Fe(+2)	0.209986	0.0184306	0.191641
Mg(+2)	73.915	0.522824	73.4223
Mn(+2)	0.119992	0.111169	8.87225e-3
F(-1)	1.11992	1.12038	0.0
O(-2)	8.85762e5	8.85593e5	529.373
Cl(-1)	379.974	380.129	0.0
C(+4)	111.118	2.91084	108.253
S(+6)	244.325	244.425	0.0
N(+5)	0.0903527	0.0903895	0.0
Si(+4)	16.1722	16.1788	0.0

Table A.4 Water concentrations after second step for softening, soda ash addition (Self production)

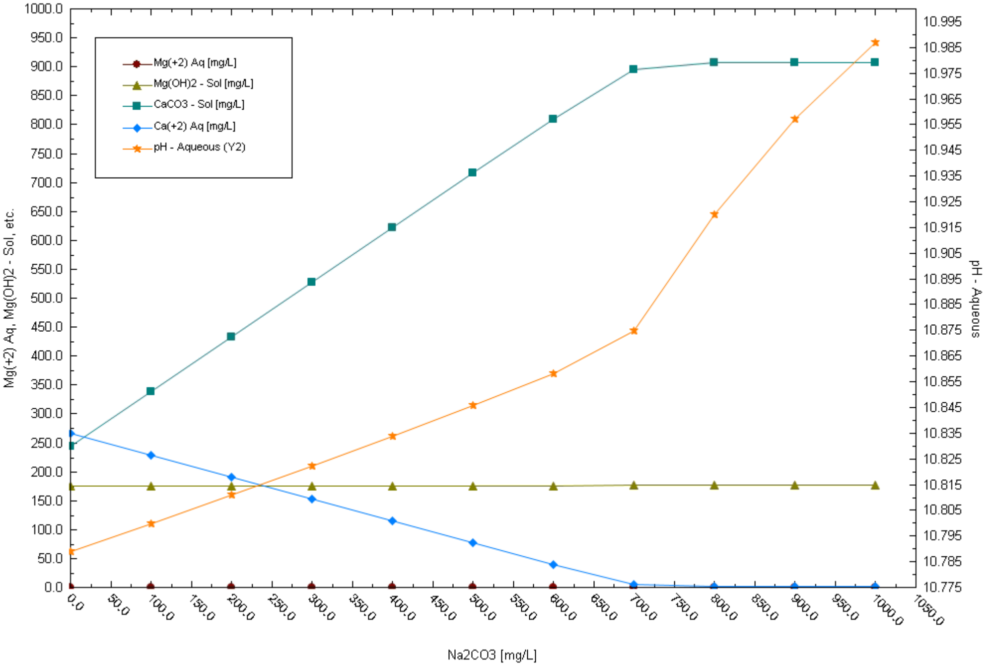
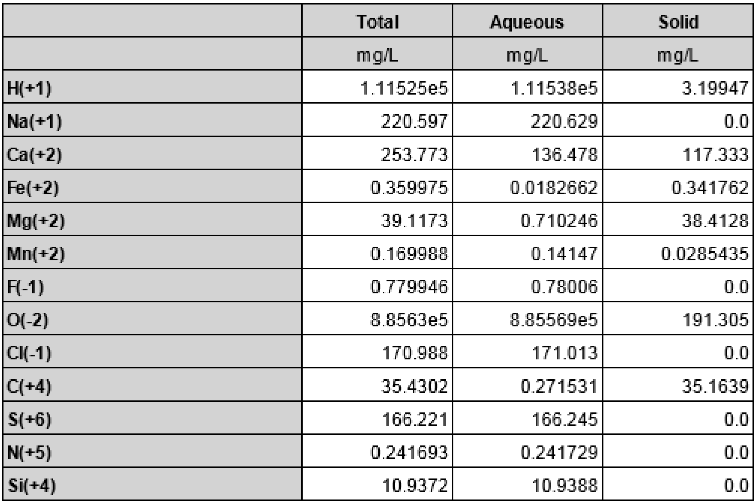


Figure A.4 Second step for softening, soda ash addition (Self production)



	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11525e5	1.11538e5	3.19947
Na(+1)	220.597	220.629	0.0
Ca(+2)	253.773	136.478	117.333
Fe(+2)	0.359975	0.0182662	0.341762
Mg(+2)	39.1173	0.710246	38.4128
Mn(+2)	0.169988	0.14147	0.0285435
F(-1)	0.779946	0.78006	0.0
O(-2)	8.8563e5	8.85569e5	191.305
Cl(-1)	170.988	171.013	0.0
C(+4)	35.4302	0.271531	35.1639
S(+6)	166.221	166.245	0.0
N(+5)	0.241693	0.241729	0.0
Si(+4)	10.9372	10.9388	0.0

Table A.5 Water concentrations after first step for softening, lime addition (Self production)

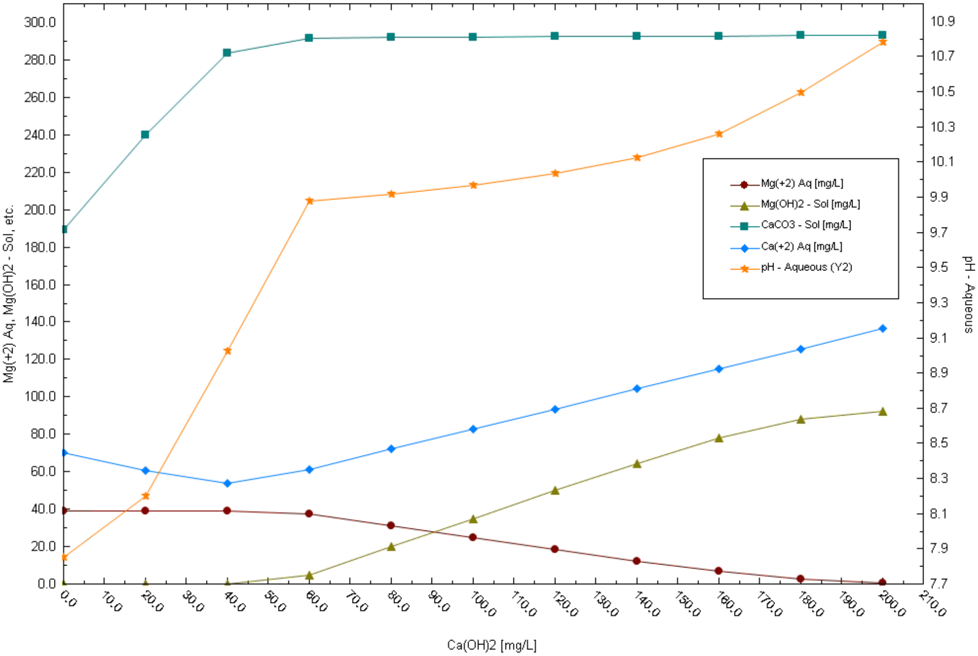


Figure A.5 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11506e5	1.11533e5	3.21215
Na(+1)	385.447	385.552	0.0
Ca(+2)	253.773	2.5081	251.334
Fe(+2)	0.359975	0.0201135	0.339959
Mg(+2)	39.1173	0.548879	38.579
Mn(+2)	0.169988	0.112149	0.0578852
F(-1)	0.779946	0.780157	0.0
O(-2)	8.85658e5	8.85546e5	352.039
Cl(-1)	170.988	171.034	0.0
C(+4)	78.4933	3.17872	75.3358
S(+6)	166.221	166.266	0.0
N(+5)	0.241693	0.241758	0.0
Si(+4)	10.9372	10.9402	0.0

Table A.6 Water concentrations after second step for softening, soda ash addition (Self production)

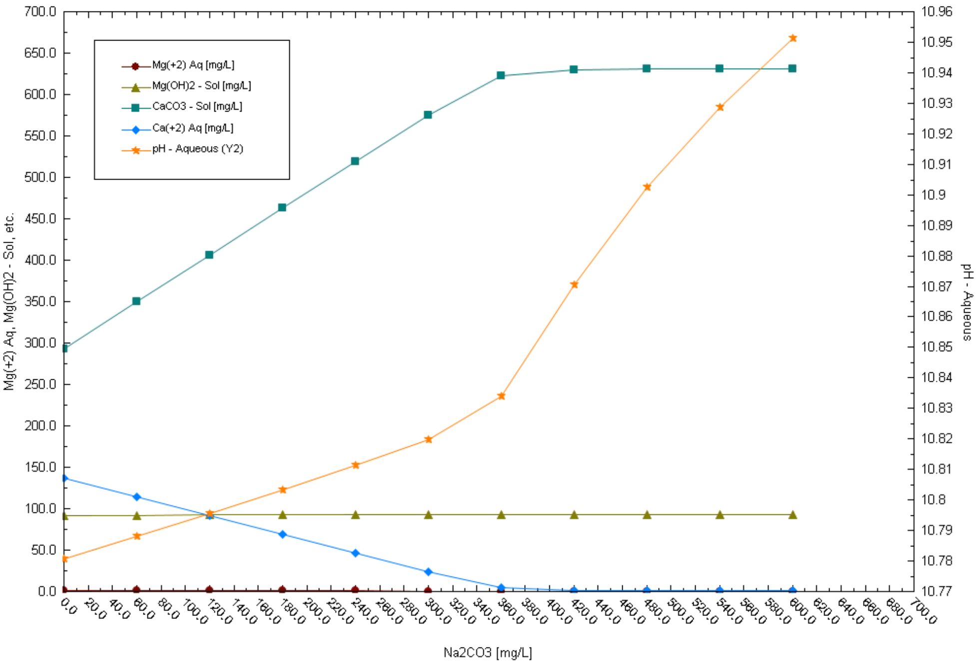


Figure A.6 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11464e5	1.11475e5	6.68185
Na(+1)	815.062	815.195	0.0
Ca(+2)	275.014	187.277	87.7816
Mg(+2)	81.3281	0.782291	80.5591
O(-2)	8.84805e5	8.84737e5	211.189
Cl(-1)	1549.96	1550.22	0.0
C(+4)	26.5739	0.270608	26.3076
Si(+4)	9.81592	9.81752	0.0

Table A.7 Water concentrations after first step for softening, lime addition (Self production)

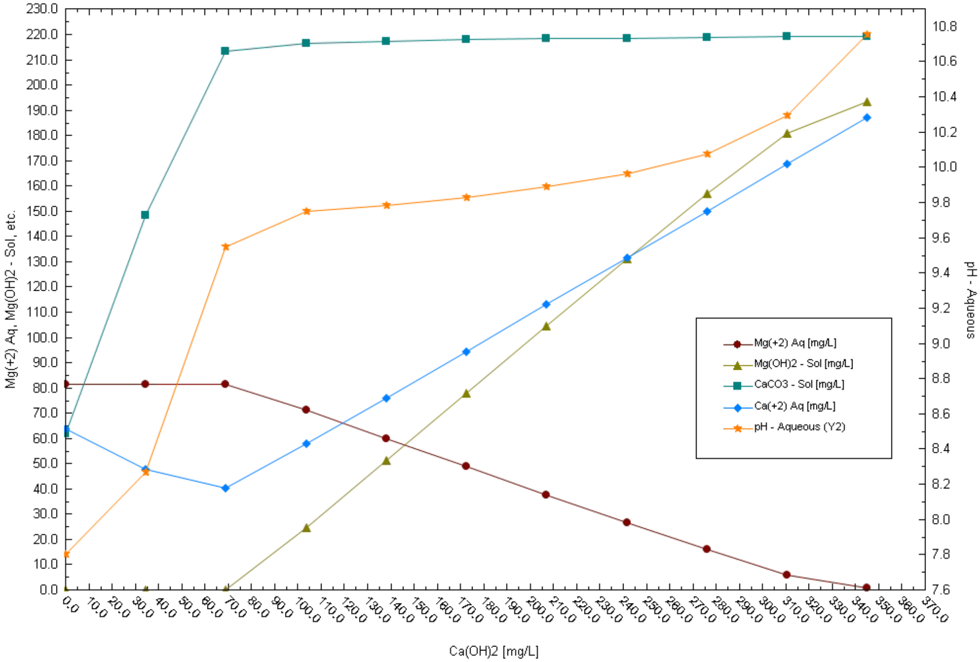


Figure A.7 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11438e5	1.11468e5	6.69517
Na(+1)	1031.97	1032.31	0.0
Ca(+2)	275.014	4.44879	270.657
Mg(+2)	81.3281	0.635415	80.7197
O(-2)	8.84825e5	8.84688e5	430.415
Cl(-1)	1549.96	1550.48	0.0
C(+4)	83.2359	2.14937	81.1141
Si(+4)	9.81592	9.81918	0.0

Table A.8 Water concentrations after second step for softening, soda ash addition (Self production)

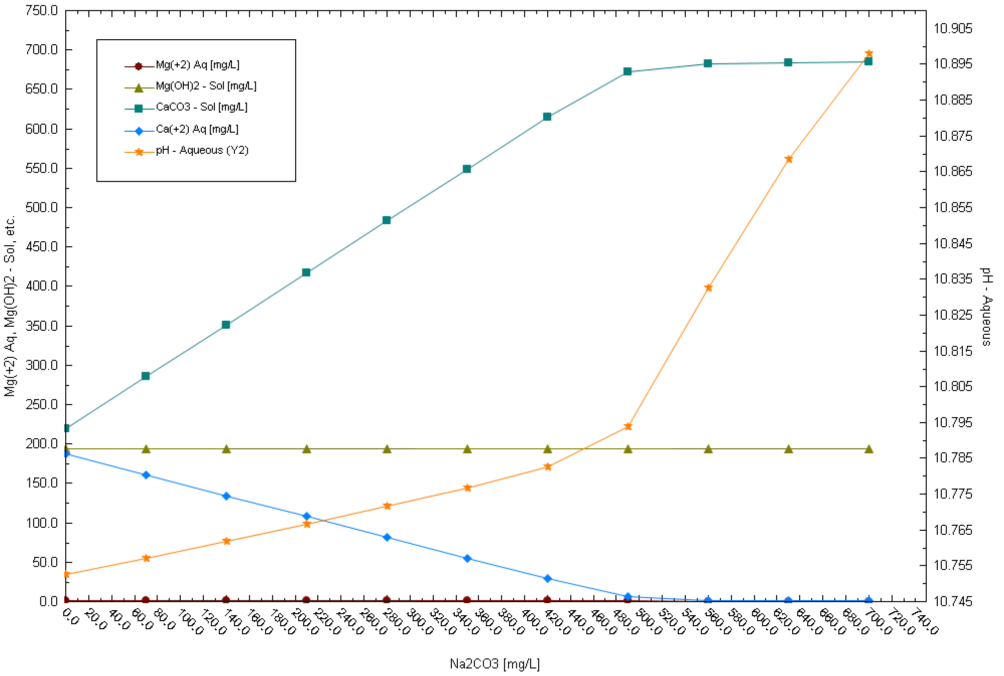


Figure A.8 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11342e5	1.11407e5	17.4843
K(+1)	259.914	260.107	0.0
Na(+1)	1789.11	1790.44	0.0
Ca(+2)	1013.71	437.104	577.353
Mg(+2)	209.931	0.482993	209.603
O(-2)	8.86017e5	8.8571e5	964.257
Cl(-1)	2067.24	2068.77	0.0
C(+4)	167.266	0.264854	167.125
P(+5)	9.12885	2.05039e-5	9.13561
S(+6)	700.748	701.268	0.0
N(+5)	22.5822	22.599	0.0
Si(+4)	33.177	33.2016	0.0

Table A.9 Water concentrations after first step for softening, lime addition (Self production)

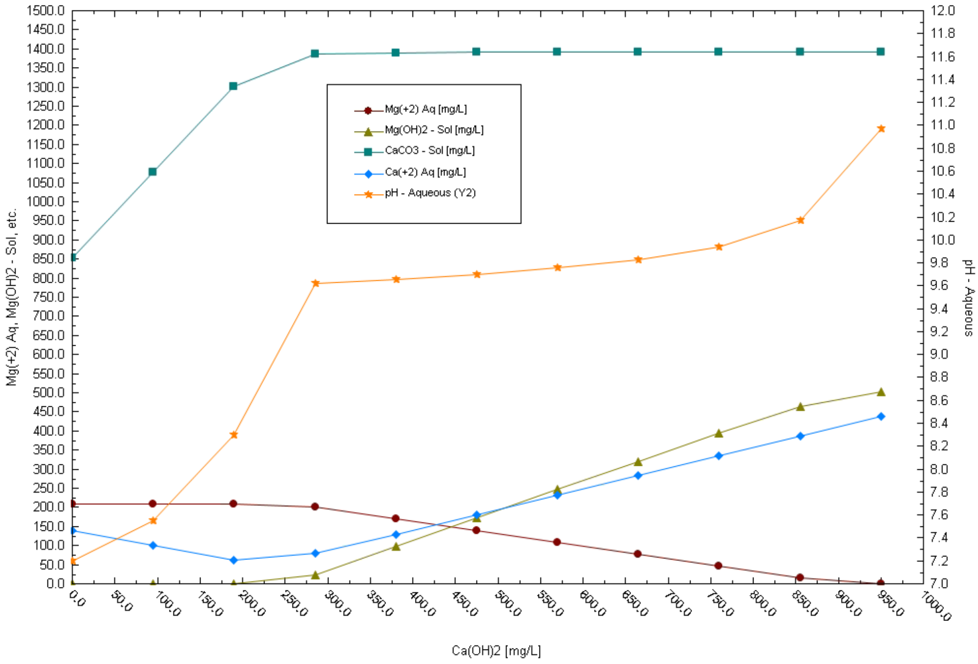


Figure A.9 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11283e5	1.11393e5	17.5044
K(+1)	259.914	260.211	0.0
Na(+1)	2439.84	2442.63	0.0
Ca(+2)	1013.71	1.15746	1013.71
Mg(+2)	209.931	0.324674	209.846
O(-2)	8.86231e5	8.85758e5	1487.17
Cl(-1)	2067.24	2069.6	0.0
C(+4)	337.252	39.7339	297.904
P(+5)	9.12885	0.0129114	9.12639
S(+6)	700.748	701.55	0.0
N(+5)	22.5822	22.6081	0.0
Si(+4)	33.177	33.2149	0.0

Table A.10 Water concentrations after second step for softening, soda ash addition (Self production)

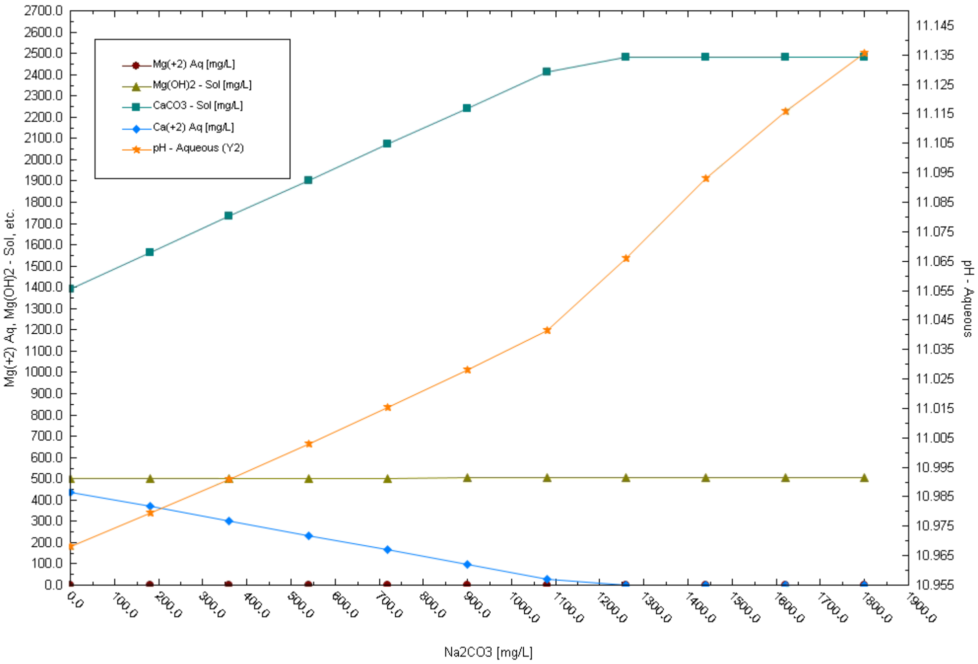


Figure A.10 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11379e5	1.11432e5	25.7141
K(+1)	19.9929	20.0071	0.0
Na(+1)	1372.41	1373.39	0.0
Ca(+2)	1144.81	716.552	429.072
Mg(+2)	309.89	0.260213	309.849
O(-2)	8.85989e5	8.85696e5	921.348
Cl(-1)	1949.31	1950.69	0.0
C(+4)	127.906	0.24958	127.747
P(+5)	1.30409	1.28219e-5	1.305
S(+6)	550.574	550.964	0.0
N(+5)	47.4215	47.4551	0.0
Si(+4)	29.438	29.4588	0.0

Table A.11 Water concentrations after first step for softening, lime addition (Self production)

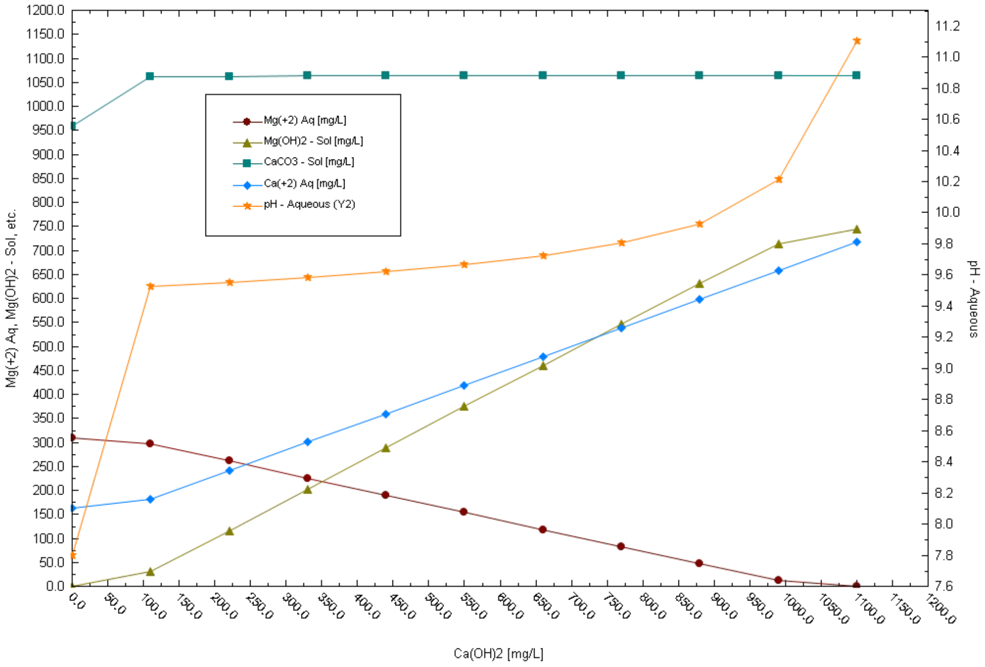


Figure A.11 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11283e5	1.1141e5	25.7387
K(+1)	19.9929	20.0203	0.0
Na(+1)	2348.5	2351.72	0.0
Ca(+2)	1144.81	1.11078	1145.27
Mg(+2)	309.89	0.167749	310.146
O(-2)	8.8625e5	8.85684e5	1779.47
Cl(-1)	1949.31	1951.98	0.0
C(+4)	382.885	41.0167	342.392
P(+5)	1.30409	9.58222e-3	1.29629
S(+6)	550.574	551.328	0.0
N(+5)	47.4215	47.4864	0.0
Si(+4)	29.438	29.4783	0.0

Table A.12 Water concentrations after second step for softening, soda ash addition (Self production)

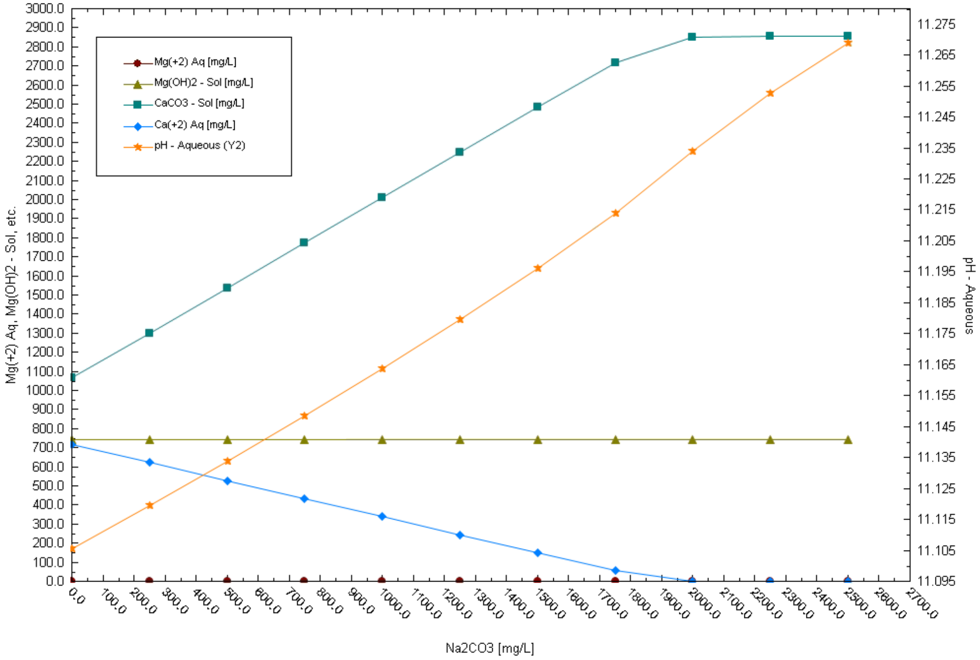


Figure A.12 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11343e5	1.11372e5	8.93709
K(+1)	45.9969	46.0127	0.0
Na(+1)	2322.71	2323.51	0.0
Ca(+2)	652.528	399.342	253.409
Mg(+2)	112.082	4.37117	107.749
F(-1)	2.9998	2.31343	0.687401
O(-2)	8.85321e5	8.85179e5	444.477
Cl(-1)	2943.73	2944.73	0.0
C(+4)	75.9783	0.276325	75.728
S(+6)	576.41	576.607	0.0
N(+5)	14.4564	14.4614	0.0
Si(+4)	52.3493	52.3672	0.0

Table A.13 Water concentrations after first step for softening, lime addition (Self production)

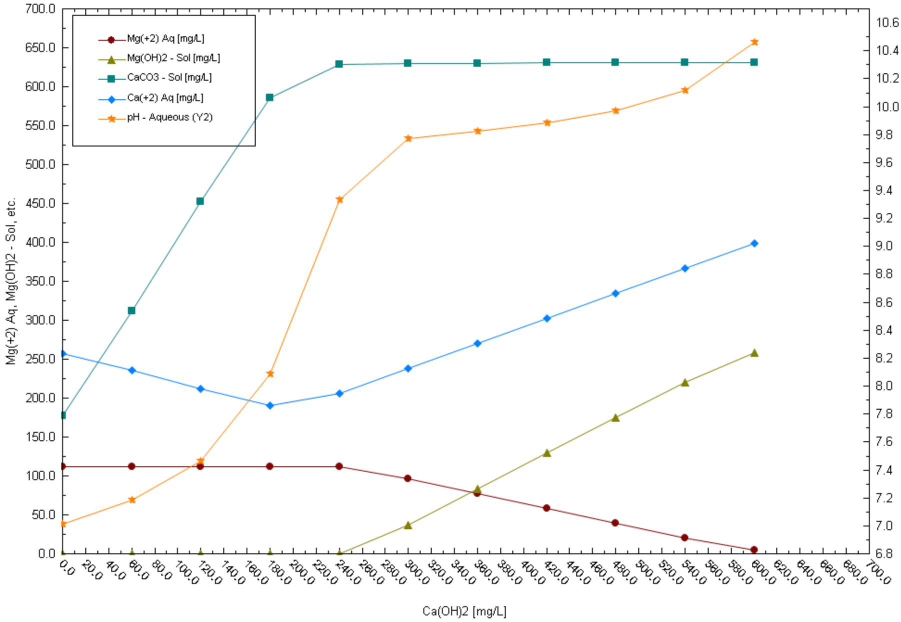


Figure A.13 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11287e5	1.11357e5	9.0455
K(+1)	45.9969	46.0295	0.0
Na(+1)	2799.91	2801.9	0.0
Ca(+2)	652.528	3.72742	649.263
Mg(+2)	112.082	3.10525	109.056
F(-1)	2.9998	3.00193	0.0
O(-2)	8.85375e5	8.85081e5	921.148
Cl(-1)	2943.73	2945.81	0.0
C(+4)	200.635	6.19674	194.58
S(+6)	576.41	576.818	0.0
N(+5)	14.4564	14.4667	0.0
Si(+4)	52.3493	52.3864	0.0

Table A.14 Water concentrations after second step for softening, soda ash addition (Self production)

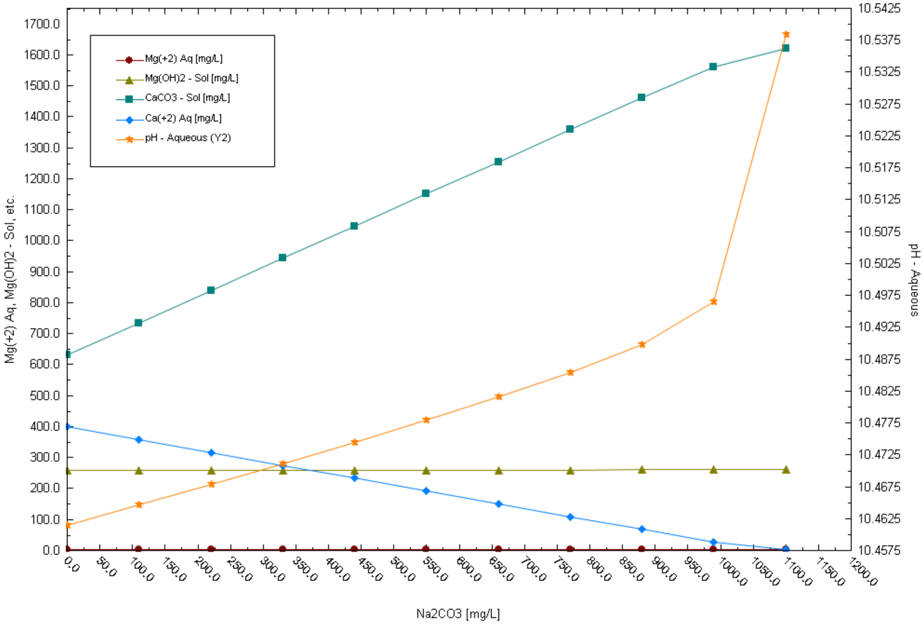


Figure A.14 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11344e5	1.11372e5	7.60097
K(+1)	45.9969	46.0119	0.0
Na(+1)	2322.71	2323.47	0.0
Ca(+2)	620.073	367.033	253.242
Mg(+2)	112.082	20.4781	91.6405
F(-1)	2.9998	2.40541	0.595371
O(-2)	8.85312e5	8.85177e5	423.185
Cl(-1)	2943.73	2944.69	0.0
C(+4)	75.9783	0.296071	75.707
S(+6)	576.41	576.598	0.0
N(+5)	14.4564	14.4612	0.0
Si(+4)	52.3493	52.3664	0.0

Table A.15 Water concentrations after first step for softening, lime addition (Self production)

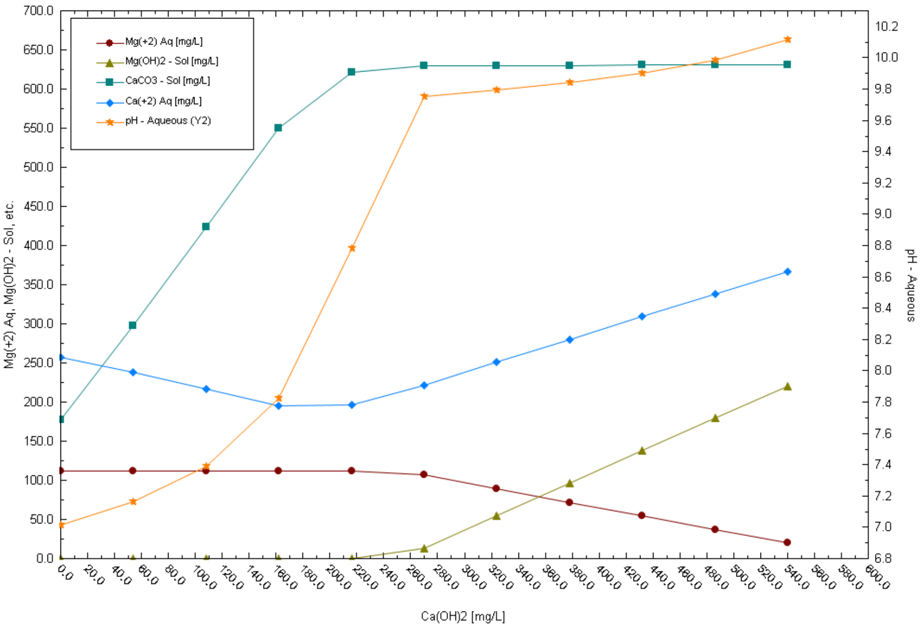


Figure A.15 First step for softening, lime addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11312e5	1.11364e5	7.62477
K(+1)	45.9969	46.0212	0.0
Na(+1)	2574.33	2575.69	0.0
Ca(+2)	620.073	148.621	471.779
Mg(+2)	112.082	20.2139	91.9274
F(-1)	2.9998	3.00138	0.0
O(-2)	8.85327e5	8.85108e5	686.039
Cl(-1)	2943.73	2945.28	0.0
C(+4)	141.706	0.39169	141.389
S(+6)	576.41	576.714	0.0
N(+5)	14.4564	14.4641	0.0
Si(+4)	52.3493	52.3769	0.0

Table A.16 Water concentrations after second step for softening, soda ash addition (Self production)

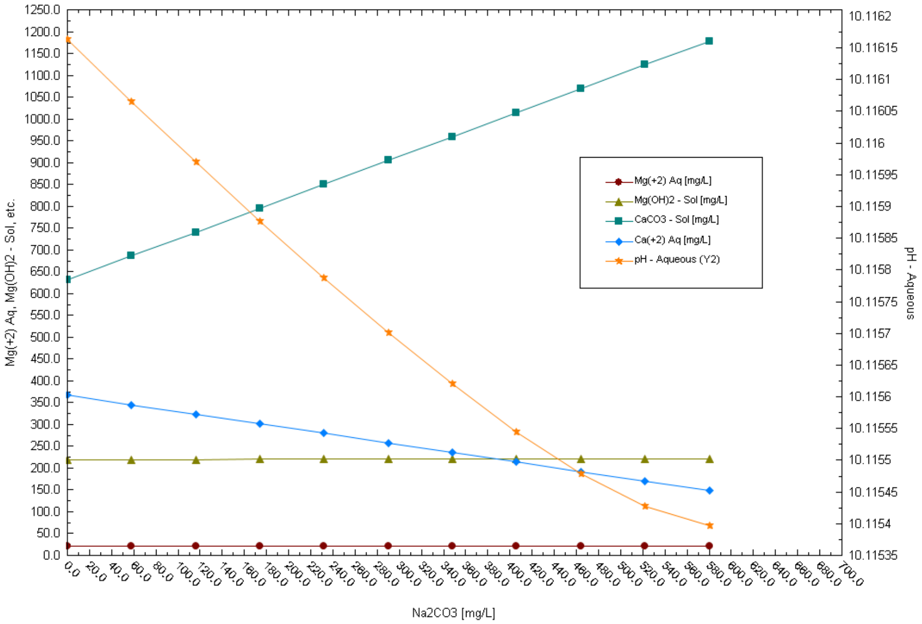


Figure A.16 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11532e5	1.11534e5	6.48827
Na(+1)	309.143	309.168	0.0
Mg(+2)	78.3714	0.152318	78.2253
O(-2)	8.85298e5	8.85265e5	102.988
Cl(-1)	332.97	332.996	0.0
Si(+4)	41.3724	41.3756	0.0

Table A.17 Water concentrations after sodium hydroxide addition (Self production)

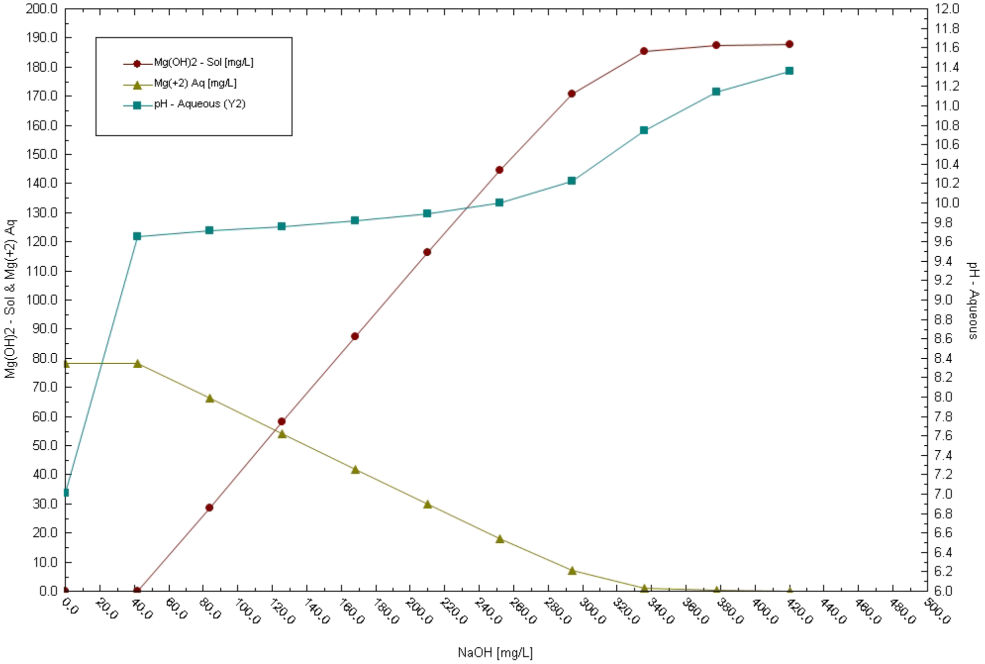


Figure A.17 Sodium hydroxide addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11536e5	1.11537e5	3.74016
Na(+1)	212.819	212.829	0.0
Mg(+2)	45.4986	0.407794	45.0929
O(-2)	8.85295e5	8.85276e5	59.3671
Cl(-1)	234.784	234.794	0.0
Si(+4)	40.4658	40.4677	0.0

Table A.18 Water concentrations after sodium hydroxide addition (Self production)

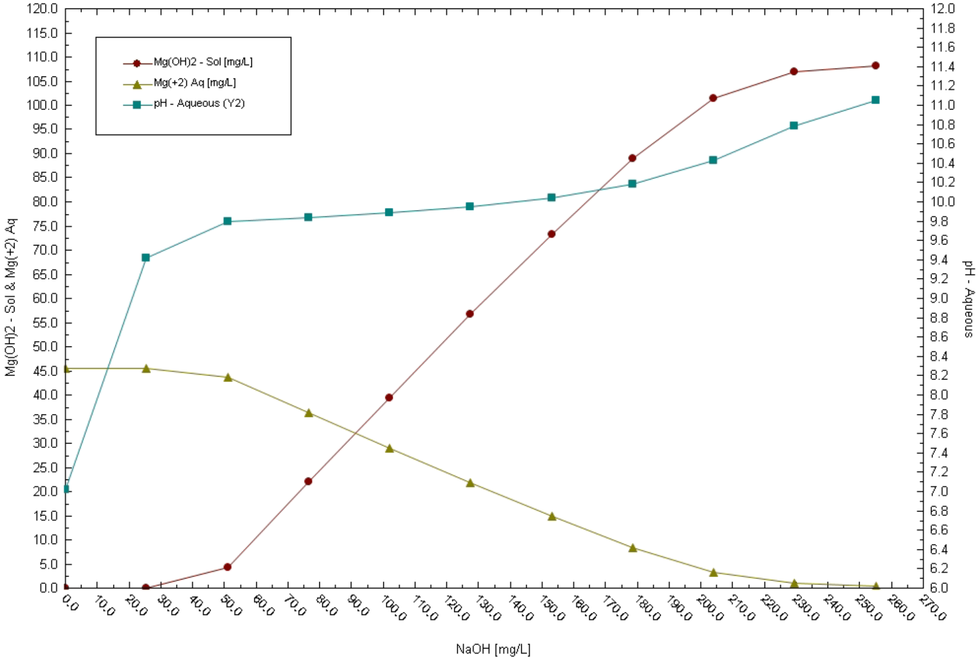
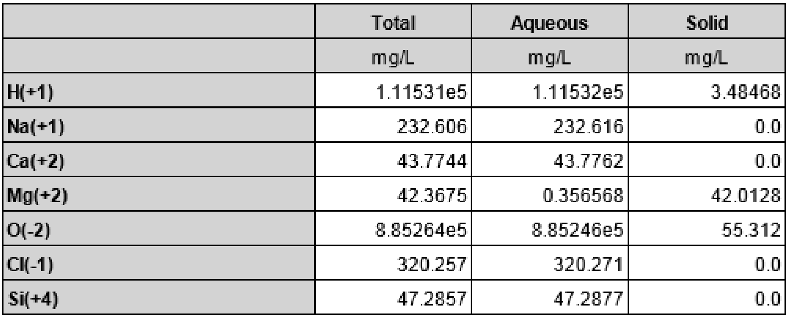


Figure A.18 Sodium hydroxide addition (Self production)



	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11531e5	1.11532e5	3.48468
Na(+1)	232.606	232.616	0.0
Ca(+2)	43.7744	43.7762	0.0
Mg(+2)	42.3675	0.356568	42.0128
O(-2)	8.85264e5	8.85246e5	55.312
Cl(-1)	320.257	320.271	0.0
Si(+4)	47.2857	47.2877	0.0

Table A.19 Water concentrations after first step for softening, caustic soda addition (Self production)

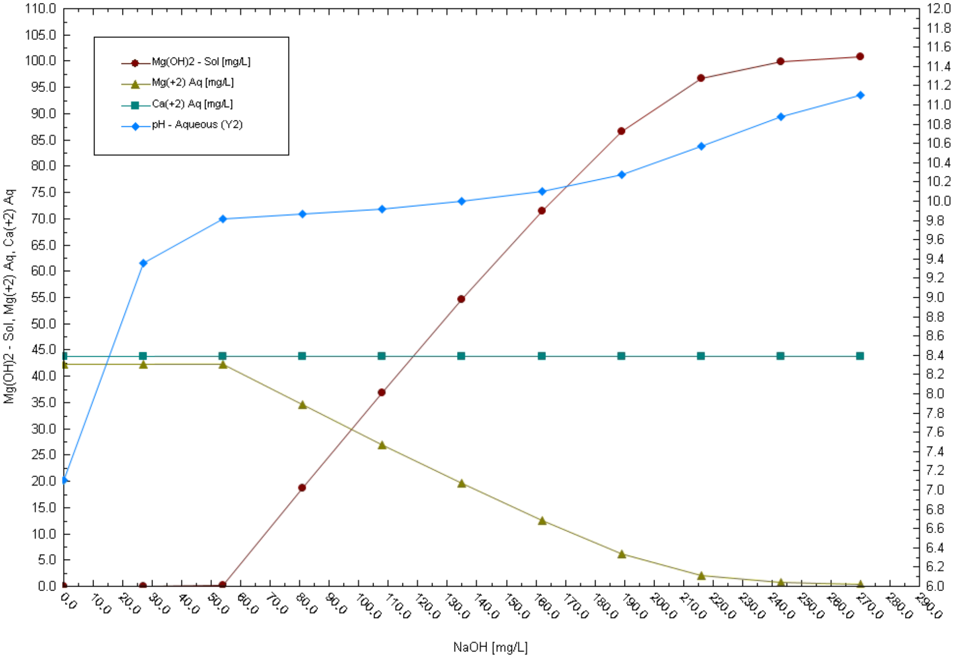
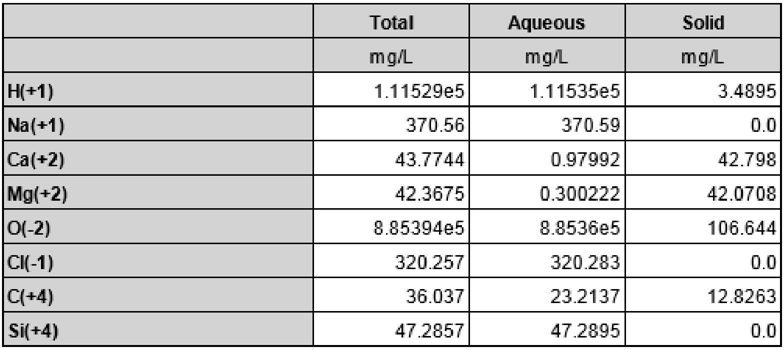


Figure A.19 First step for softening, caustic soda addition (Self production)



	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11529e5	1.11535e5	3.4895
Na(+1)	370.56	370.59	0.0
Ca(+2)	43.7744	0.97992	42.798
Mg(+2)	42.3675	0.300222	42.0708
O(-2)	8.85394e5	8.8536e5	106.644
Cl(-1)	320.257	320.283	0.0
C(+4)	36.037	23.2137	12.8263
Si(+4)	47.2857	47.2895	0.0

Table A.20 Water concentrations after second step for softening, soda ash addition (Self production)

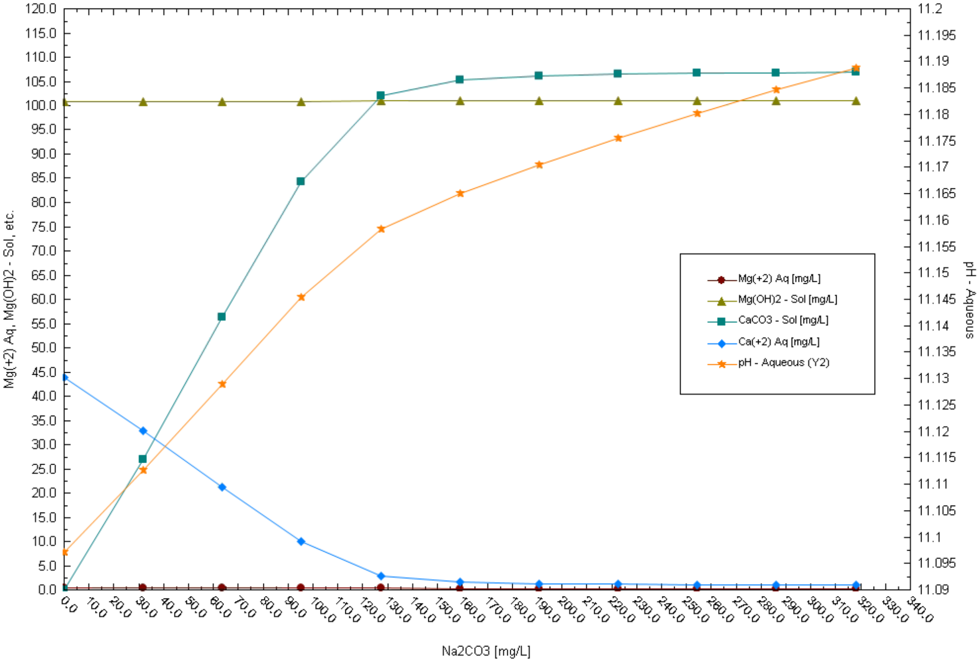
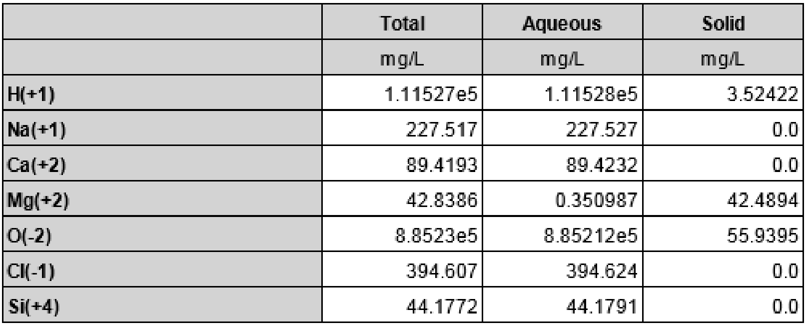


Figure A.20 Second step for softening, soda ash addition (Self production)



	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11527e5	1.11528e5	3.52422
Na(+1)	227.517	227.527	0.0
Ca(+2)	89.4193	89.4232	0.0
Mg(+2)	42.8386	0.350987	42.4894
O(-2)	8.8523e5	8.85212e5	55.9395
Cl(-1)	394.607	394.624	0.0
Si(+4)	44.1772	44.1791	0.0

Table A.21 Water concentrations after first step for softening, caustic soda addition (Self production)

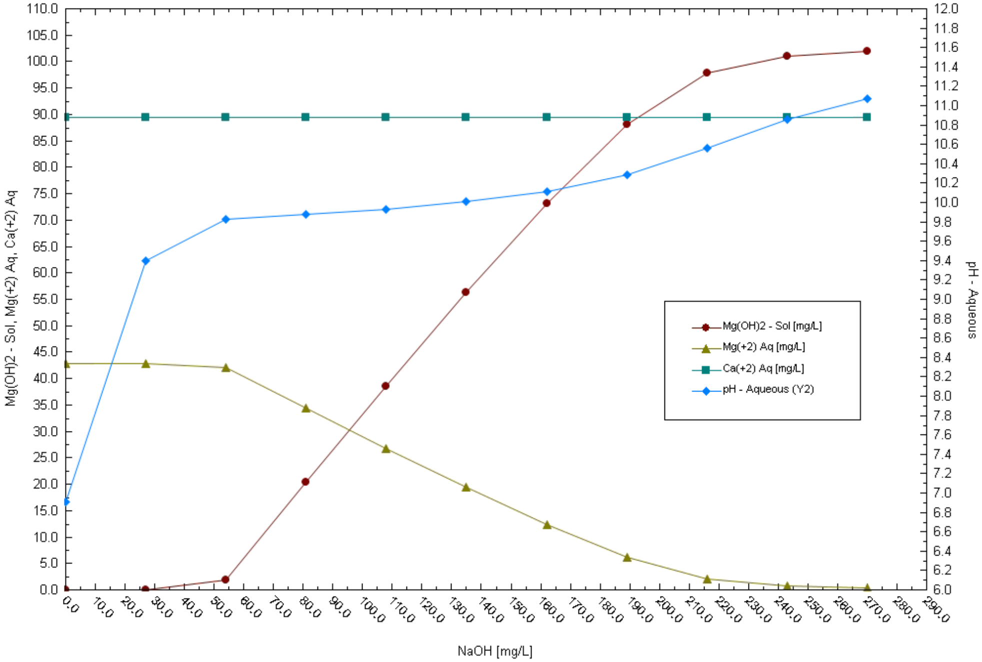


Figure A.21 First step for softening, caustic soda addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11521e5	1.11531e5	3.53136
Na(+1)	457.44	457.497	0.0
Ca(+2)	89.4193	0.926039	88.5044
Mg(+2)	42.8386	0.268332	42.5756
O(-2)	8.85424e5	8.85373e5	162.048
Cl(-1)	394.607	394.656	0.0
C(+4)	60.0617	33.545	26.5242
Si(+4)	44.1772	44.1827	0.0

Table A.22 Water concentrations after second step for softening, soda ash addition (Self production)

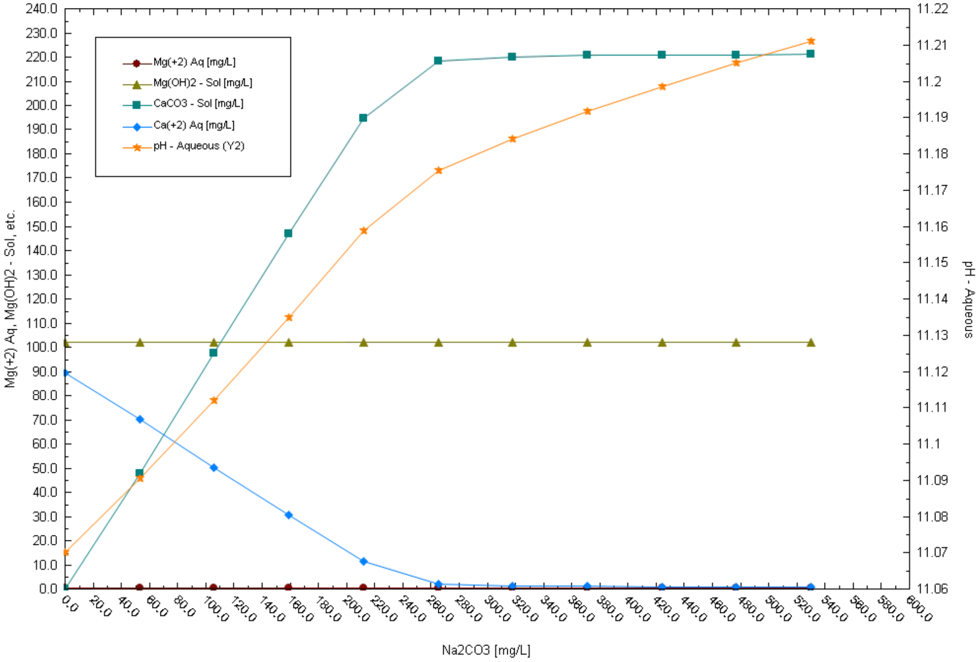


Figure A.22 Second step for softening, soda ash addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11522e5	1.11524e5	3.75268
Na(+1)	233.254	233.264	0.0
Ca(+2)	132.713	132.719	0.0
Mg(+2)	45.8285	0.586774	45.2439
O(-2)	8.85199e5	8.8518e5	59.5659
Cl(-1)	488.774	488.797	0.0
Si(+4)	47.6814	47.6836	0.0

Table A.23 Water concentrations after first step for softening, caustic soda addition (Self production)

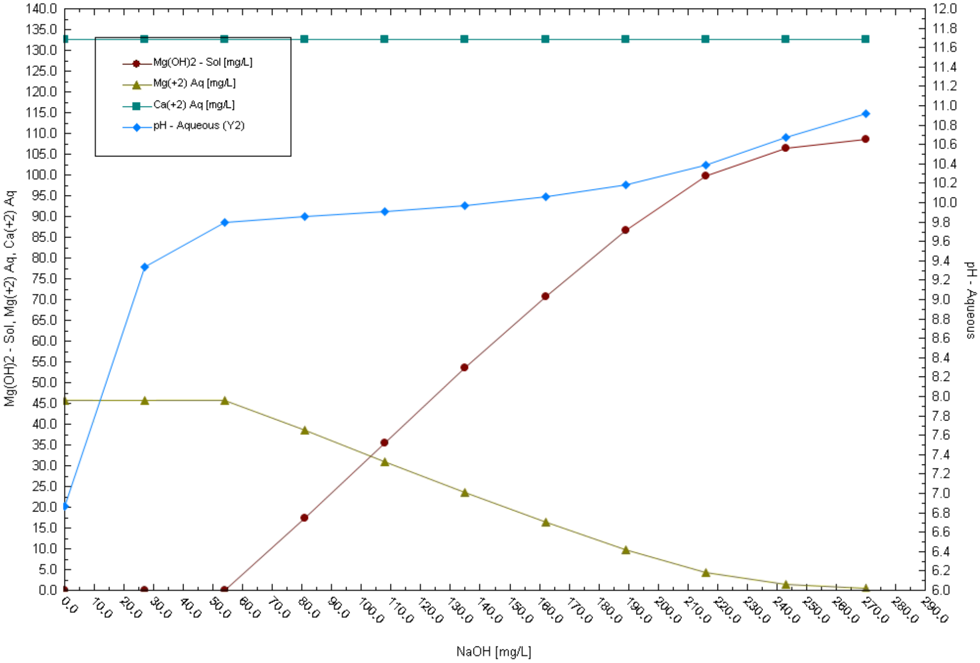


Figure A.23 First step for softening, caustic soda addition (Self production)

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11511e5	1.11526e5	3.77244
Na(+1)	554.278	554.371	0.0
Ca(+2)	132.713	0.897209	131.838
Mg(+2)	45.8285	0.354064	45.4821
O(-2)	8.85447e5	8.85377e5	217.772
Cl(-1)	488.774	488.856	0.0
C(+4)	83.8598	44.3627	39.5112
Si(+4)	47.6814	47.6894	0.0

Table A.24 Water concentrations after second step for softening, soda ash addition (Self production)

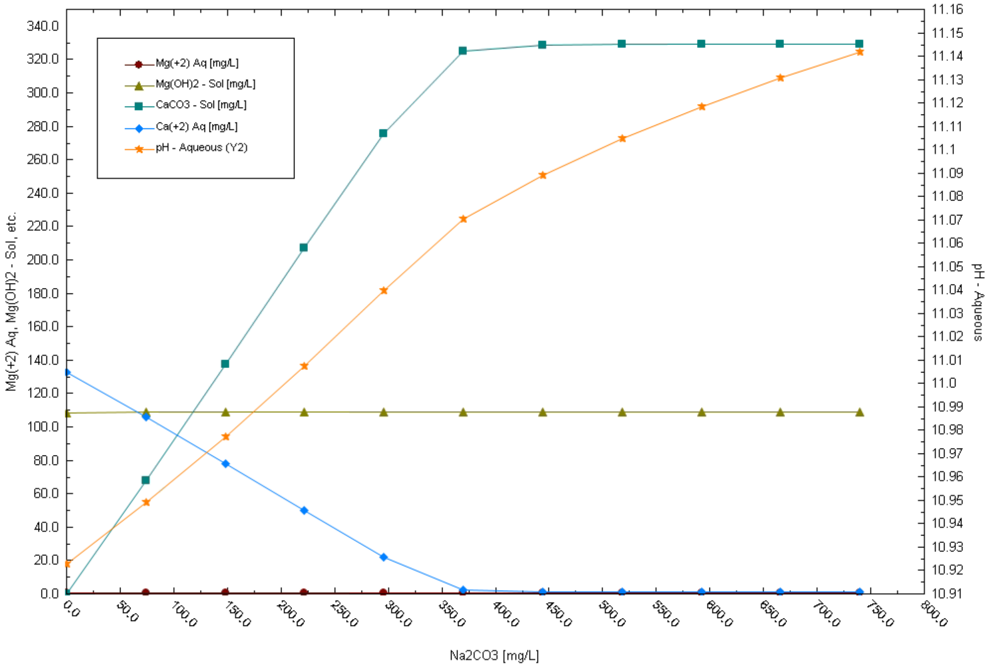
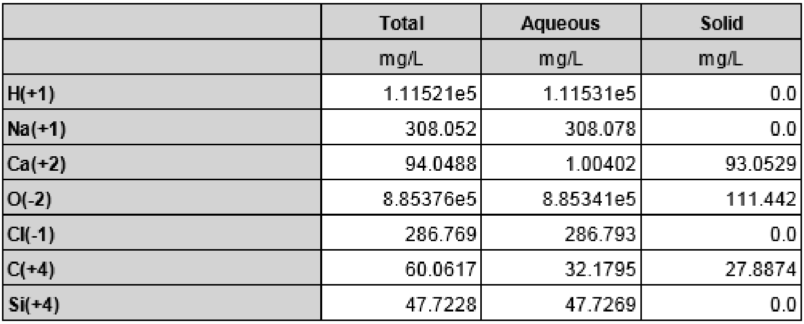


Figure A.24 Second step for softening, soda ash addition (Self production)



	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H(+1)	1.11521e5	1.11531e5	0.0
Na(+1)	308.052	308.078	0.0
Ca(+2)	94.0488	1.00402	93.0529
O(-2)	8.85376e5	8.85341e5	111.442
Cl(-1)	286.769	286.793	0.0
C(+4)	60.0617	32.1795	27.8874
Si(+4)	47.7228	47.7269	0.0

Table A.25 Water concentrations after soda ash addition (Self production)

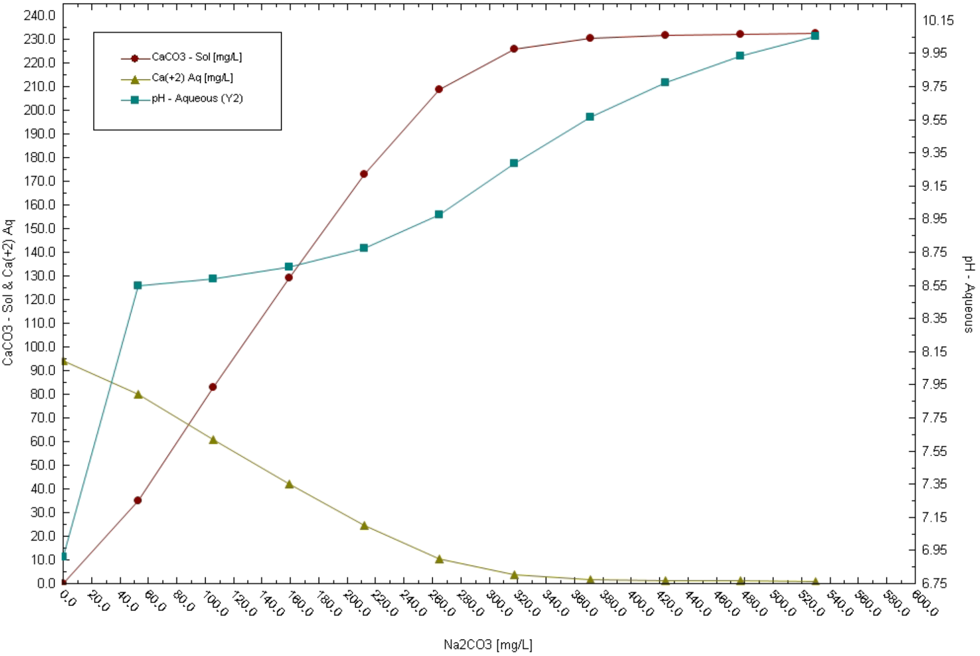


Figure A.25 Soda ash addition (Self production)