Chapter 6  Water Treatment – Lime Softeners

The Application
This chapter expands the mixing process presented in Chapter 1. The Mixed Waste is sent to a softener to remove Ca, Mg, Fe, and Al. The remaining liquid is neutralized.

Formulating the Process

The Mixed Waste stream contains a water, solid, and gas phase. It flows into a reaction tank with lime and soda ash that are used to raise pH and to increase the carbonate concentration. The higher pH and carbonate results in CaCO$_3$, Mg(OH)$_2$, Al(OH)$_3$, and Fe(OH)$_3$ precipitation. These solids are removed in the clarifier unit. The remaining liquid is neutralized for and sent to a downstream process.

The required procedure is to expand the chemistry model to include the lime and soda ash additives. Then the additional units and streams are added.

Chemistry Model

Open the existing Case file
The work on this case started in Chapter 1. You were instructed to save the file. Open it now.

✓ Open the file, Water Treatment Softening Process
Adding additional components to the model
The first step is to add lime (CaO) and soda ash (Na2CO3) to the chemistry model.

- Click on the Chemistry tab.
- Enter CaO and Na2CO3 to the list.

![Image](image.png)

Figure 6-2 – Adding CaO and Na2CO3 to the Chemistry Inflows List

- Return to the flowsheet view.

Building the Process
The following instructions are designed to take us on a tour through some of the interesting features of the ESP Process Analysis facilities.

![Image](image.png)

Figure 6-3 - The Water Softening process created in this chapter

Adding new process blocks
Start by adding the new unit operations:

- Click on the Mixer object in the library, and drag it to the right of the Adiabatic mixer.
- Label it Softener Reactor.
- Next, click on the Separator object in the library and drag it to the right of the Softener reactor.
- Label it Clarifier.
- Next, click on the Neutralizer object and drag it to the right of the Settler.
- Label it pH Neutralizer.

Adding new streams
Next, add link existing stream and add new ones.

- Link the Mixed Waste stream to the inlet side of the Softener Reactor block.
- Click on the Add Stream button in the menu and add two streams to the Softener Reactor (mixer) inlet.
✓ Add a stream to the Softener reactor outlet and link it to the Clarifier (separator) inlet.
✓ Add three streams to the Clarifier outlet; vapor, solid and liquid. Link the liquid stream to the pH neutralizer (Neutralizer) inlet.
✓ Add a streams to the neutralizer inlet top and one to the bottom.
✓ Press the ESC key or click the Add stream button a second time to deactivate the action.

**Labeling and Editing the new streams**
✓ Label the eight streams as follows. Use the above screenshot for identification

<table>
<thead>
<tr>
<th>Lime</th>
<th>Soda Ash</th>
<th>Reactor Outlet</th>
<th>Clarifier Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vent</td>
<td>Clarifier Sludge</td>
<td>20% HCl</td>
<td>Neutralized Liquid</td>
</tr>
</tbody>
</table>

**Entering the Lime stream data**
✓ Click on the Lime stream.
✓ Enter a Stream Amount of 80 mol/hr.

The lime stream composition is based on mass fraction, and so the Inflow units need to be changed from mol/hr to mass fraction. This is done through the Units Manager window.

✓ Click on the hyperlinked units at the header of the Inflows category.
✓ Change the Inflows units from Moles to Mass Fraction. Press OK.

![Figure 6-4 Changing the units of the Lime stream](image)

✓ Enter a CaO value of 100 mass %.

![Figure 6-5 The Lime Stream Composition. Note the inflow units are changed to Mass%](image)

✓ Change the Set Phase setting to Solid Only. This is in the Advanced Options section at
the bottom of the Lime stream Properties panel.

![Figure 6-6 Entering the Lime Inflow rate](image)

By changing the Set Phase to Solid only, the software will compute the stream’s total enthalpy and heat capacity, but will not attempt to compute any phase properties. This change ensures that the calculation proceed without any problems.

**Soda Ash inflow stream**
- Click on the Soda Ash stream.
- Enter a Stream Amount of 100 mol/hr.
- Change the inflow units to Mass Fraction (mass %).
- Enter a Na2CO3 value of 100 mass %.
- Change the Set Phase setting to Solid Only.

![Figure 6-7 Entering the Soda Ash composition and inflow rate](image)

The soda ash stream has similar setting to the lime stream. In many instances, lime and soda ash are slaked with process water before entering the reactor. We will look into that scenario in a later chapter.

**20% HCl Inflow stream**
- Click on the 20% HCl stream entering the pH Neutralizer.
- Enter a Stream Amount of 50 mol/hr.
- Change the Inflow units from moles to mass fraction (mass %).
- Enter 80% H2O and 20% HCl.
**Reviewing the Clarifier settings**

- Click on the Clarifier block to access its Properties panel.

![Properties panel](Figure 6-9 The Clarifier Properties panel. It contains four sections, Inlets, Outlets, Equilibrium calculations and Advanced options)

The Properties panel contains four sections. The Inlets and Outlets section display the streams attached to the block. The Equilibrium Calculation section contain the calculation settings. The Advanced Options section contains the Chemistry model selection (to be explained in later chapters).

There are three outlet streams, and each outlet will contain a single phase. This means that the vapor will not contain mist or dust, the liquid will not contain gas bubbles or suspended solids, and the solids will not be wet. Also, the Clarifier is set to run adiabatically.

There are no properties/settings to adjust in this block.

**Changing the pH Neutralizer Block settings**

- Click on the pH Neutralizer block to access its Properties panel.
The purpose of this block is to add sufficient quantities of the 20% HCl stream to set the Neutralized liquid output stream pH=8. The 50 moles of you entered when creating the 20% HCl stream, is therefore an initial guess. This Neutralizer block will adjust this value until the target pH of 8 is achieved. This block, therefore, acts as a mixer, a pH controller and as an HCl valve.

- Click on the Calculation Type option in the Equilibrium Calculation section and change to Fix pH.
- Enter a pH of 8.0.

**Calculate and Review**

The flowsheet is ready for calculation. This is also a good time to save the file.

- Save your file.
- Press the Calculate button

The calculation should complete within seconds. If you receive an Error warning, please look at the Error tab located at the bottom of the window. It will tell you what step you may have missed.

There are now eleven streams in the process. With that number it is easier to review the results using the Report or by using the Callout tables. You will start by reviewing the reports.

- Click on the Report-1 tab. This is the default report.
- Click on the Add all streams action link

The table that appears contains the properties and composition of each stream.

Unnecessary or redundant streams, namely the lime, soda ash, 20% HCl and vent are removed in a manner similar to adding streams.

- Review the 20% HCl inflow stream, look at the Apparent moles and the volume.
Review the Moles, Apparent row; 196.4 moles of acid were added, and not the 50 moles that you entered earlier. Notice that there are two Moles values: Moles, True and Moles, Apparent. The Moles, True sums the cations (H+) and anions (Cl-, OH-) separately. By comparison the Moles Apparent is simply the molecular HCl and H2O. Thus the True moles is always equal or greater than the apparent moles (it can be equal if there is no ionization—for example when dissolving carbon monoxide in water).

You will now reduce the size of the report to make it easier to review.

- Click the Remove link on the 20% HCl, Lime, Soda Ash, and Vent columns to remove them.

This reduces the table size, and leaves only the seven streams. Values to be reviewed include the sludge flow rate and the pH of each stream. Note also Clarifier Liquid and Sludge temperature. It has increased to 46°C.

One purpose of the softening unit is to remove total calcium and magnesium (hardness) from the water as solids (sludge). You can review the extent of Mg and Ca removal from the process, including the amount that still remains in the Neutralized liquid. These results are in a section called MBG Totals, Combined, located towards the bottom of the report. The term, MBG is Material Balance Group, or the element with a specific oxidation state. The section, MBG Totals, Combined contains the total amount of each element that is in the stream. By comparison, the section, MBG Totals, Solids contains the elements that make up the solids phase of that stream.

- Remove all the streams except for the Reactor Outlet, Clarifier Sludge, and Neutralized Liquid.
- Scroll down the report to the MBG Totals, Combined section.
- Compare the Ca(+2) and Mg(+2) flow of the Mixed Waste and neutralized liquid.

The reactor outlet stream is a mixed phase, containing water, solids, the clarifier sludge is all solids, and the neutralized liquids is nearly all liquid.
The Mg\(^{2+}\) is converted to Mg(OH)\(_2\) by raising the mixed waste pH to 9.3 using CaO. Adding CaO increases the Ca\(^{2+}\) content. Thus, Na\(_2\)CO\(_3\) is added to remove the existing and added Ca\(^{2+}\) as CaCO\(_3\). The total dissolved Ca\(^{2+}\) decreases from 129.8 mol/hr to 7.8 mol/hr and the dissolved Mg\(^{2+}\) decreases from 14.9 mol/hr to 1.5 mol/hr. The optimum amount of CaO and Na\(_2\)CO\(_3\) is investigated in the next chapter.

✓ Save your file.

Including entrained water in the sludge and settling it out

The sludge stream is 100% solids. It contains no entrained water. This does not exist in practice, since clarifier sludge may contain up to 90% water. The Separator unit, where the sludge and supernatant were separated, can accept instructions to entrain water in the solids, thereby creating a more representative sludge product. This will be performed now.

**Setting the Separator Entrainment value**

✓ Click on the report tab and view the sludge stream. It is currently 100% solids.

✓ Return to the flowsheet and select the Clarifier unit.

✓ Select the Entrainment arrow button

✓ Set the Liquid in Solid (g/g) value to 9 -  

This instructs the software to set the water to Sludge ratio to 9:1, that is, to make the Clarifier Sludge stream 90% water.

✓ Calculate and view the Phase flows section of the Clarifier Sludge in the report.
There is now 114 kg/hr process water entrained with the sludge. This is about 20% of the total liquids, and it needs to be separated from the solids and returned to the process. In water treatment operations, a significant fraction of the liquid can be separated using coagulating and settling. The software contains a settler block that can mimic this step. Please note, that this block does not compute the physical-chemical process of coagulation, settling, and separation. Rather it separates based on user-entered separation values, and these values are presumed to be obtained from plant performance data.

**Adding a Settler block**

The purpose of a settler block is to separate a process stream into a liquid and solid streams with a fixed fraction of liquids remaining with the solids a fixed fraction of solids flowing with the liquid as suspended solids. In this scenario, you will split 100% of the solids to the “Solids” stream and split 80% of the liquids to the “Liquid” stream. Thus, 80% of the liquids entering the settler will decant.

- Click on the Settler block in the Library and drag it below and to the right of the Clarifier unit.
- Label the block “Sludge Settler”.
- Link the Clarifier Sludge stream to the inlet.
- Click on the New Stream button in the Toolbar and add two outlet streams to the sludge settler.
- Label the liquid stream “Settler Liquid”.
- Label the solid stream “Settler Solids”.
- Link the Settler Liquid stream to the inlet of the pH Neutralizer.
Figure 6-16 – Clarifier sludge is processed in a Sludge Settler

- Click on the Sludge Settler object.
- Click on the Outlet Split Parameters button in the Properties panel.

The window that appears contains two splits, Liquid phase and Solid phase. Each phase can split to two outlets.

Figure 6-17 – Sludge Settler Parameters

The split flows can be set to volume, mass, or moles. In this case, 100% of the solids go with the Solids stream outlet (Settler Solids), and 80% of the liquid goes with the Effluent stream outlet (Decanted Liquid).

- Set the fractions in the settler to match the values shown in the image above.
- Recalculate.
- Click on the Report. Change the stream selection to display the Reactor Outlet, Settler Solids, Neutralized Liquid, vent, and 20% HCl.

These streams represent the mass balance around the clarifier, settler, and neutralized liquid.

- Review the Phase Flow section and then MBG Totals, Combined section.

There is 563 kg/hr liquid exiting the neutralization tank and 24 kg/hr liquid exiting with the Settler solids. The settler solids stream is now about 60% liquid.
Adding a filter press to recover remaining liquid

The last part of this scenario is to recover the remaining water. It is performed using a filter press. The Filter object in Flowsheet ESP is very similar to the Settler. It differs in that it does not contain the individual solid phase split option that is part of the settler.

- Click on the Filter object in the Library and drag it below and to the right of the Settler block.
- Label the object Filter Press.
- Drag the Settler Solids stream to the filter Press inlet.
- Click on the Add Stream button and add a stream to the Filter press liquid and solid exits.
- Label the liquid stream Filtrate. Label the solids stream Filter Cake.
Click on the Filter Press object and click on the Outlet Split Edit button.

- Set the Liquid split settings to 0.92 (filtrate stream) and 0.08 (Solids stream).
- Set the Solids Split to 0 and 1.

As with the Settler, the final water content in the filter cake is computed from these settings. If the filter cake water content is known, then a separator can be used instead of the filter.

- Calculate and view the Results tab.
- Change the columns to display the Reactor Outlet, Filter Cake, and Neutralized liquid.
The filter cake flows at 12.5 kg/hr solid and 1.8 kg/hr liquid; ~13% liquid in the filter cake. Now, a small fraction of the liquid is lost to disposal.

✓ Save the file. It will be used in the next chapter.

Summary
This chapter expanded on the water treatment process with the addition of a softening/clarifier unit, a pH neutralizer, and filtration. The lime and soda ash inlet rates were set manually, by reviewing the results and adjusting the Stream Amount cell. This action can be performed automatically by using controllers and manipulating (valve) units. You will add these units in the next chapter.