SIMULATION OF LIME-SODA SOFTENING

By Li-Shiang Liang¹, Irvine W. Wei² and Henry G. Sideropoulos³

INTRODUCTION

Chemical requirement and product composition for lime-soda softening is usually calculated using the bar diagram method and its variations (3,5). Lime-soda ash softening is assumed to be capable of reducing calcium and magnesium to empirically determined "practical limits" of 0.6 - 0.8 meq/l and 0.2 meq/l, respectively. For calcium removal, the required lime and soda ash dosages are calculated by stoichiometry. For magnesium removal, an empirically determined excess of typically 1.0 - 1.25 meq/l is added to the stoichiometric lime requirement.

Other methods based on the Caldwell-Lawrence diagrams(3,4) take into account the inter-relationships between pH and concentrations of carbonic species and calcium at saturation in CaCO₃. The curves in the diagrams are generated by solution of equilibrium equations. The equilibrium constants can be calculated as functions of the ionic strength and the temperature.

Magnesium and sulfate ions in the raw water will affect the equilibrium concentrations of calcium and carbonic species in the softened water by the formations of uncharged ion pairs. It is the aim of this paper to present a computer model of lime-soda softening, taking into account the effects of magnesium and sulfate and to compare the results of computer simulation with laboratory experiments.

COMPUTER MODEL

Major Assumptions - A schematic of a model for a single-stage lime-soda softener is shown in Fig. 1. The assumptions made are:

Figure 1. Single-Stage Lime-Soda Softening.
1. The reaction tanks are perfectly mixed.

2. The concentrations of the reacting chemical species attain steady-state values in the reaction tanks and can be determined by equilibrium-based calculations. Experimental work by Alexander and MClanahan (1) and by Merril and Jorden (6) indicate that steady-state in lime-induced reactions is reached in the order of 10-25 minutes; reaction time of over 25 minutes is achievable in lime-soda ash softeners.

3. There is no transfer of CO₂ with the atmosphere.

4. The water temperature remains constant throughout the process.

**Equations** - The model calculates the equilibrium concentrations of the following species: Ca²⁺, CaOH⁺, CaHCO₃⁺, Mg²⁺, MgOH⁺, MgHCO₃⁺, SO₄²⁻, HCO₃⁻, CO₃⁻, H⁺, OH⁻, CaCO₃⁰⁻, MgCO₃⁰⁻, CaSO₄⁰⁻, MgSO₄⁰⁻, H₂CO₃, Ca₁₋ₓMgₓCO₃(S), Mg(OH)₂(S). The superscript '₀' denotes uncharged ion pairs and the suffix '(S)' the precipitated solid species.

The possible chemical reactions between the above species are as follows:

\[ \begin{align*}
H^+ + OH^- & \rightleftharpoons H_2O \tag{1} \\
H^+ + HCO_3^- & \rightleftharpoons H_2CO_3 \tag{2} \\
H^+ + CO_3^{2-} & \rightleftharpoons HCO_3^- \tag{3} \\
Ca^{2+} + OH^- & \rightleftharpoons CaOH^+ \tag{4} \\
Ca^{2+} + HCO_3^- & \rightleftharpoons CaHCO_3^- \tag{5} \\
Ca^{2+} + CO_3^{2-} & \rightleftharpoons CaCO_3 \tag{6} \\
(1-x)Ca^{2+} + xMg^{2+} + CO_3^{2-} & \rightleftharpoons Ca_{1-x}Mg_xCO_3(S) \tag{7} \\
Ca^{2+} + SO_4^{2-} & \rightleftharpoons CaSO_4 \tag{8} \\
Mg^{2+} + OH^- & \rightleftharpoons MgOH^+ \tag{9} \\
Mg^{2+} + HCO_3^- & \rightleftharpoons MgHCO_3^- \tag{10} \\
Mg^{2+} + CO_3^{2-} & \rightleftharpoons MgCO_3^0 \tag{11} \\
Mg^{2+} + SO_4^{2-} & \rightleftharpoons MgSO_4^0 \tag{12} \\
Mg^{2+} + 2OH^- & \rightleftharpoons Mg(OH)_2(S) \tag{13}
\end{align*} \]

With regard to Equation 7, the mole fraction of MgCO₃ in the precipitated
magnesian calcite depends primarily on the mole ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ in the aqueous phase (10). Benjamin et al (2) correlated the experimental results of several previous investigators with the following equations:

$$pK_{\text{spm}} = pK_{\text{spo}} - 1.744x$$  \hspace{1cm} (14)

$$x = \frac{1}{1 + 50(Ca^{2+})/(Mg^{2+})}$$

where $K_{\text{spo}} = \text{solubility product of calcite (pure CaCO}_3\text{).}$

$K_{\text{spm}} = \text{solubility product of magnesian calcite.}$

( ) denotes activities.

The equilibrium constants are functions of temperature and are calculated by equations in App. II. Mass action expressions for each reaction include the effect of ionic strength. For this purpose the activity coefficients for dissolved species are calculated by:

$$\log f_i = \frac{AZ_i^2 I^{1/2}}{1 + B_i I^{1/2} + b_i I}$$  \hspace{1cm} (8)

where $A,$ $B = \text{functions of the absolute temperature, density and dielectric constant of the water}$

$I = \text{ionic strength} = \frac{1}{2} \sum \frac{Z_i^2 C_i}{C_i}$

$Z_i = \text{ionic charge}$

$C_i = \text{molar concentration}$

$a_i,$ $b_i = \text{parameters calculated from experimental data.}$

Equations for $A$ and $B$ and the parameters $a_i$ and $b_i$ are given in App. II.

The remaining equations necessary are the equation of electroneutrality:

$$0 = [H^+] + [\text{CaOH}^+] + [\text{CaHCO}_3^+] + 2[\text{Ca}^{4+}] + [\text{MgOH}^+]$$

$$+ [\text{MgHCO}_3^+] + 2[\text{Mg}^{4+}] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}]$$

$$- 2[\text{SO}_{4}^{2-}] - [\text{OH}^-] - R$$  \hspace{1cm} (16)

where $R = \text{normality of non-reacting negatively charged species} - \text{normality of non-reacting positively charged species}; \text{ e.g. } R = [\text{Cl}^-] + [\text{NO}_3^-] - [\text{Na}^+] - [\text{K}^+]$. 

-4-
and the mass balance equations for calcium, magnesium, carbon and sulfur:

\[
[Ca]_T = [Ca^{2+}] + [CaOH^+] + [CaHCO_3^+] + [CaCO_3^0] + [CaSO_4^0] + (1-x) [Ca_{(1-x)}Mg_xCO_3(s)]
\]  
(17)

\[
[Mg]_T = [Mg^{2+}] + [MgOH^+] + [MgHCO_3^+] + [MgCO_3^0] + [MgSO_4^0] + x[Ca_{1-x}Mg_xCO_3(s)]
\]  
(18)

\[
[C]_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [CaHCO_3^+] + [CaCO_3^0] + [MgHCO_3^+] + [MgCO_3^0] + [Ca_{1-x}Mg_xCO_3(s)]
\]  
(19)

\[
[S]_T = [SO_4^{2-}] + [CaSO_4^0] + [MgSO_4^0]
\]  
(20)

where \([ ]\) denotes concentrations and \([ ]_T\) denotes total concentration of an element.

The mass action equations can be used to rearrange the four mass balance equations and the electroneutrality equation into 5 non-linear simultaneous equations in 5 unknowns. The procedure for solving the equations and calculating the equilibrium concentrations is described in App. IV.

In the computer model the addition of chemicals and the removal of precipitated solids by settling are accounted for by changes in the total concentration of calcium, magnesium, carbon and sulfur and by changes in the concentration of precipitated solids and in the parameter R as shown in Table 1.

EXPERIMENTS

Water Analyses - Synthetic waters with systematic variations in composition were batch softened in the laboratory. Complete description of 18 experimental runs is given in Reference 8. In this paper, five runs are discussed as examples; the water analyses are given in Table 2, along with the calculated ionic strengths. Expts. 1 and 2 differ mainly in the concentration of the non-reacting salt KCl and therefore in the ionic strength. Expts. 3-5 investigate the effect of magnesium and sulfate on softening of water with relatively high ionic strength and temperature.
TABLE 1. PARAMETERS AFFECTED BY SELECTED OPERATIONS

<table>
<thead>
<tr>
<th>Chemical Addition</th>
<th>([\text{Ca}]_T)</th>
<th>([\text{Mg}]_T)</th>
<th>([\text{C}]_T)</th>
<th>([\text{S}]_T)</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)₂</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Settling</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>
### Table 2. Water Analyses (Units in Millimoles/L except pH and T)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2.51</td>
<td>2.61</td>
<td>2.49</td>
<td>2.49</td>
<td>2.51</td>
</tr>
<tr>
<td>Mg</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.26</td>
<td>1.24</td>
</tr>
<tr>
<td>K</td>
<td>2.0</td>
<td>52.0</td>
<td>103.75</td>
<td>103.75</td>
<td>153.75</td>
</tr>
<tr>
<td>HCO₃</td>
<td>2.0</td>
<td>2.0</td>
<td>3.75</td>
<td>3.75</td>
<td>3.75</td>
</tr>
<tr>
<td>Cl</td>
<td>5.01</td>
<td>55.21</td>
<td>104.97</td>
<td>107.50</td>
<td>107.50</td>
</tr>
<tr>
<td>SO₄</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>25.0</td>
</tr>
<tr>
<td>pH</td>
<td>8.0</td>
<td>7.8</td>
<td>8.2</td>
<td>8.1</td>
<td>8.4</td>
</tr>
<tr>
<td>T(°C)</td>
<td>24</td>
<td>21</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

Calculated Ionic Strength
9.53  59.8  111  115  190
Experimental Procedure - Solid hydrated lime was added directly to 1 liter samples of the synthetic water and the samples were mixed for 20 minutes. Half of each sample was removed and settled for 20 minutes. The remainder was mixed for an additional 100 min and settled. Transfer of CO₂ with the atmosphere was prevented by plastic caps on the vessels. After settling, the supernatant was filtered through glass fibre filters. Before and after filtration the pH and the concentrations of total dissolved calcium in the supernatant were measured. Total dissolved calcium was determined by EDTA titration.

Experimental Results - Figs. 2-6 show for the five experimental runs the concentration of total dissolved calcium in the filtrate vs. filtrate pH and the lime added vs. filtrate pH. The experimental data is for 20 minutes of mixing; data for 120 minutes of mixing does not differ significantly (8). The theoretical curves are the results of the computer model.

DISCUSSION

If Figs. 2-6 the theoretical curves and experimental data show that there exists an optimum pH in the reaction tank for each water at which the total calcium remaining in solution is a minimum. The theoretical curves of lime added vs. pH predict that the buffering capacity is also a minimum at the optimum pH. Experimental and theoretical values for the minimum achievable dissolved calcium concentration, the lime dosage required and the corresponding pH are tabulated in Table 3. The experimental values are estimates from interpolation between data points. Results of calculations using the Bar Diagram method are included for comparison.

Computer simulations of Expts. 1 and 2 predict that the ionic strength difference of 50 moles/l between the two experiments will have insignificant effect on the minimum dissolved calcium concentration. The prediction is supported by the experimental data.

Computer simulation of Expts. 3-5 predicts that magnesium and sulfate will form uncharged ion pairs with carbonate and calcium, respectively, and thereby decrease the concentrations of free calcium and carbonate ions.
Figure 2. Experiment 1.
Figure 3. Experiment 2.
Figure 4. Experiment 3.
Figure 5. Experiment 4.
Figure 6. Experiment 5.
### TABLE 3. SUMMARY OF RESULTS OF EXPERIMENTS, COMPUTER SIMULATION AND BAR DIAGRAM METHOD

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$[\text{Ca}<em>\text{D}]</em>{\text{min}}$</th>
<th>Lime</th>
<th>$(\text{pH})_{\text{opt}}$</th>
<th>$[\text{Ca}<em>\text{D}]</em>{\text{min}}$</th>
<th>Lime</th>
<th>$(\text{pH})_{\text{opt}}$</th>
<th>$[\text{Ca}<em>\text{D}]</em>{\text{min}}$</th>
<th>Lime</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.1</td>
<td>9.0</td>
<td>1.55</td>
<td>1.0</td>
<td>9.5</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>1.6</td>
<td>1.2</td>
<td>9.5</td>
<td>1.55</td>
<td>1.05</td>
<td>9.7</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>2.0</td>
<td>9.5</td>
<td>0.76</td>
<td>1.80</td>
<td>9.5</td>
<td>1.01</td>
<td>1.88</td>
</tr>
<tr>
<td>4</td>
<td>0.95</td>
<td>1.9</td>
<td>9.4</td>
<td>0.84</td>
<td>1.78</td>
<td>9.3</td>
<td>1.01</td>
<td>1.88</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>1.9</td>
<td>9.5</td>
<td>0.90</td>
<td>1.70</td>
<td>9.5</td>
<td>1.01</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Note: $[\text{Ca}_\text{D}]_{\text{min}}$ = minimum dissolved calcium concentration achievable in millimole/1.

Lime = millimole/1 of lime necessary to achieve $[\text{Ca}_\text{D}]_{\text{min}}$.

$(\text{pH})_{\text{opt}}$ = pH in reaction tank corresponding to $[\text{Ca}_\text{D}]_{\text{min}}$. 
which can precipitate as CaCO₃. The limited experimental data is not conclusive. Simulation of Expts. 4 and 5 predicts that the total dissolved calcium and the lime requirement increase sharply as the pH is raised above the value at which magnesium hydroxide precipitates. The sharp increase is confirmed by the data.

Figs. 2-6 show that computer simulation can qualitatively predict the relationships between total dissolved calcium, lime requirement and filtrate pH. The numerical disagreement between the theory and experiment may be due to errors in the equilibrium constants used in the computer calculations.

Table 3 shows that the Bar Diagram method consistently underestimates the lime requirement and overestimates the minimum achievable concentration of dissolved calcium in the experiments.

PRACTICAL APPLICATIONS

For lime softening the five synthetic waters in Table 2, computer simulation does not offer any clear-cut advantage over the Bar Diagram method in predicting the residual calcium concentration and the lime dosage.

Further investigation of the effects of ion pairs and ionic strength on lime-soda softening is currently underway. Synthetic waters simulating cooling water in closed-cycled power plant cooling systems will be softened in the laboratory and the results compared with computer simulation.

Modifications to the equilibrium constants may be necessary to develop an accurate computer model of lime-soda softening. Such a model will provide an optimum pH at which the reaction tank should be maintained to achieve minimum dissolved calcium concentration. The pH measurement can be used in a feedback loop to control the rate of chemical addition.

CONCLUSIONS

A computer model for lime-soda softening has been developed based on the solution of simultaneous chemical equilibrium equations. Qualitatively the results of computer simulation agree well with data from lime softening of synthetic waters in the laboratory. Further research is necessary to improve the numerical accuracy of the model.
APPENDIX I. REFERENCES


APPENDIX II. THERMODYNAMIC EQUILIBRIUM CONSTANTS

The equilibrium constants are given by an equation of the form:

\[
\log K = a \frac{b}{T} + cT - d \log T, \text{ with } T \text{ in } ^\circ\text{K}, \text{ where:}
\]
APPENDIX III. PARAMETERS USED IN ACTIVITY COEFFICIENTS

Activity coefficients are calculated as follows:

\[ \log f = - \frac{AZ^2T^{1/2}}{1 + B\alpha^{1/2}} + bI \]

\[ A = \frac{1.8248 \times 10^6}{(180T - 0.342T^2)^{3/2}} \text{ in units of } \left( \text{moles l}^{-1} \right)^{-1/2} \]

\[ B = \frac{50.292}{(180T - 0.342T^2)^{1/2}} \text{ in units of } \left( \text{moles l}^{-1} \right)^{-1/2} (\text{Å})^{-1} \]

\( Z = \text{ionic charge} \)
\( I = \text{ionic strength} = \frac{1}{2} \sum Z_i^2C_i \text{ summed for all charged species including non-reacting species such as Na}^+ \) and \( \text{Cl}^- \).
\( T = \text{absolute temperature, °K.} \)
\( a = \text{parameter, "hydrated ion size"}, \text{ in units of } \text{Å}^{-1} \)
\( b = \text{parameter in units of } \left( \text{moles l}^{-1} \right)^{-1} \)
APPENDIX IV. CALCULATIONAL PROCEDURES

Three possible saturation states are assumed:
- Unsaturated in both magnesian calcite and Mg(OH)$_2$
- Saturated in magnesian calcite but not in Mg(OH)$_2$
- Saturated in both magnesian calcite and Mg(OH)$_2$

The equations of mass action, mass balance and electroneutrality can be arranged into a set of five nonlinear simultaneous equations in five unknowns for each saturation state.

For each saturation state, the calculational procedures are as follows:

1. A set of initial values for the concentrations of the chemical species and the ionic strength is assumed; the equilibrium constants and activity coefficients are calculated.
2. The five nonlinear simultaneous equations are linearized by Taylor series expansion and solved by iteration using the Newton-Raphson method.

3. The concentration of the remaining chemical species are calculated using the mass action equations.

4. The ionic strength and the activity coefficients are recalculated.

5. Step 2 is repeated until the successive values of the ionic strength and the chemical species of interest converge to a specified criteria.