CHEMISTRY OF LIME-SODA SOFTENING OF COOLING WATER

by

Li-Shiang Liang, David J. Goldstein and Irvine W. Wei

This paper summarizes the results to date of an ongoing project to compare computer simulation of lime-soda ash softening with data from laboratory experiments.

Lime-soda ash softening is a well established water treatment process. For municipal water supply softening is used to reduce the total hardness in the raw water to optionally 75-85 mg/l as CaCO$_3$ and the magnesium hardness to less than 40 mg/l as CaCO$_3$. The chemical reactions involved are usually described by the following set of stoichiometric equations:

$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$

$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$

$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3 + MgCO_3 + 2H_2O$

$MgCO_3 + Ca(OH)_2 = CaCO_3 + Mg(OH)_2$

$2NaHCO_3 + Ca(OH)_2 = CaCO_3 + Na_2CO_3 + 2H_2O$

$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$

$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$

Stoichiometry alone provides insufficient information for design of the softening process. The potential reduction in calcium and magnesium must be determined by chemical equilibrium calculations and/or empirically based methods.

The bar diagram method and its variations are well documented. 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 take into account the inter-relationships between pH and concentrations of carbonic species and calcium at saturation in CaCO$_3$. 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.

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LIME-SODA SOFTENING OF COOLING WATER

In an open recirculating cooling system incorporating a cooling tower, heat is dissipated by evaporation and by convective heat transfer with the air. Evaporation concentrates the dissolved solids in the cooling water; a bleed stream called the blowdown is discharged from the cooling system to prevent the solids concentrations from increasing to levels at which scaling of the heat transfer surfaces may occur. Makeup water is added to replace water lost by evaporation, blowdown and drift. Chemicals to inhibit corrosion, scaling, fouling and biological growth are often added to the cooling water.

Lime-soda ash softening has been used to remove calcium, magnesium, silica, phosphates and alkalinity from cooling water in order to prevent scaling of the heat exchangers by precipitated solids such as calcium carbonate, calcium sulfate, magnesium hydroxide, magnesium silicates and calcium orthophosphates. Softening of the makeup and/or a sidestream from the recirculating water, as shown in Figure 1, will allow a reduction in the blowdown rate necessary. In the extreme case of zero blowdown, dissolved solids which are not removed by precipitation in the softener, such as chloride, sulfate and sodium, will be removed from the cooling system only with the water lost by drift and with the softener sludge. The reader is referred to References 6-12 for detailed discussion of sidestream softening theory, equipment, economics and operating experience.

The motivation behind the current work is to develop a computer model of lime-soda ash softening to be used particularly in the design of sidestream softeners for cooling tower systems. Recirculating cooling waters differ from most natural waters in having higher temperatures (typically 30-45°C for a steam-electric power plant) and higher concentrations of dissolved solids and, therefore, higher ionic strengths. Furthermore, cooling waters may contain scale inhibiting chemicals and dispersants which may interfere with the softening process.

COMPUTER MODEL

A schematic of a model for a two-stage lime-soda ash softener is shown in Figure 2*, along with a schematic of the calculational steps which have been programmed both on a desk top calculator and in Fortran IV. The program contains several input points at which, for example, chemical reagents may be added or the fraction of precipitated solids removed by settling may be specified.

*In most currently available softening equipment, the chemical reaction and solids precipitation in each softening stage are carried out in the same vessel.
Figure 1. Possible equipment configurations for lime-soda ash softening of cooling water.
Figure 2. Schematic of the process model and the calculation steps in the computer model.

MB = Mass balance
EC = Equilibrium concentration in reactors
SS = Solids separation in settlers
The major assumptions made in our present program are:

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\(^\text{15}\) and by Merril and Jorden\(^\text{16}\) 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 \(\text{CO}_2\) with the atmosphere.

4. The water temperature remains constant throughout the process.

The major part of our computer program is devoted to calculation of the equilibrium concentrations of the following species:

Charged dissolved species: \(\text{Ca}^{2+}, \text{CaOH}^+, \text{CaHCO}_3^+, \text{Mg}^{2+}, \text{MgOH}^+, \text{MgHCO}_3^+\), \(\text{SO}_4^{2-}, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{H}^+, \text{OH}^-\)

Uncharged dissolved species: \(\text{CaCO}_3^0, \text{MgCO}_3^0, \text{CaSO}_4^0, \text{MgSO}_4^0, \text{H}_2\text{CO}_3\)

Solid species: \(\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3(S), \text{Mg(OH)}_2(S)\)

Silica can be removed in lime-soda ash softeners by adsorption onto precipitated magnesium hydroxide, and will be included in future modifications to our program.

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O})</td>
<td>(1)</td>
</tr>
<tr>
<td>(\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3)</td>
<td>(2)</td>
</tr>
<tr>
<td>(\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-)</td>
<td>(3)</td>
</tr>
<tr>
<td>(\text{Ca}^{2+} + \text{OH}^- \rightarrow \text{CaOH}^+)</td>
<td>(4)</td>
</tr>
<tr>
<td>(\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaHCO}_3)</td>
<td>(5)</td>
</tr>
<tr>
<td>(\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3^0)</td>
<td>(6)</td>
</tr>
<tr>
<td>((1-x)\text{Ca}^{2+} + x\text{Mg}^{2+} + \text{CO}<em>3^{2-} \rightarrow \text{Ca}</em>{1-x}\text{Mg}_x\text{CO}_3(S))</td>
<td>(7)</td>
</tr>
</tbody>
</table>
Ca$^{+2} +$ SO$_4^{-2} \rightarrow$ CaSO$_4$ \hspace{1cm} (8)

Mg$^{+2} +$ OH$^- \rightarrow$ MgOH$^+$ \hspace{1cm} (9)

Mg$^{+2} +$ HCO$_3^-$ $\rightarrow$ MgHCO$_3$ \hspace{1cm} (10)

Mg$^{+2} +$ CO$_3^{-2} \rightarrow$ MgCO$_3$ \hspace{1cm} (11)

Mg$^{+2} +$ SO$_4^{-2} \rightarrow$ MgSO$_4$ \hspace{1cm} (12)

Mg$^{+2} + 2OH^- \rightarrow$ Mg(OH)$_2$(s) \hspace{1cm} (13)

Reaction (7) is of particular interest. When calcium carbonate precipitates in the form of calcite, magnesium may be incorporated into the crystal lattice. The mole fraction of MgCO$_3$ in the resulting magnesian calcite depends primarily on the mole ratio of Mg$^{+2}$/Ca$^{+2}$ in the aqueous phase$^{13}$. The mass action expression for reaction (7) can be written as$^{13}$:

\[(Ca^{+2})_{1-X} (Mg^{+2})^X (CO_3^{-2}) = K_{spm}\] \hspace{1cm} (1)

where \((\ )\) denotes activities

K$_{spm}$ = solubility product for magnesian calcite which varies with X

\(X = \text{mole fraction of MgCO}_3 \text{ in the lattice}\)

Benjamin et al$^{14}$ correlated the experimental results of several previous investigators with the following equations:

\[pK_{spm} = pK_{spo} - 1.744X\] \hspace{1cm} (2)

\[X = \frac{1}{1 + 50(Ca^{+2})/(Mg^{+2})}\] \hspace{1cm} (3)

where K$_{spo}$ = solubility product of calcite (pure CaCO$_3$). From equation (1) we can define an apparent solubility product K$_{sp1}$ for CaCO$_3$ as follows:

\[(Ca^{+2})(CO_3^{-2}) = K_{spm} \frac{(Ca^{+2})^X}{(Mg^{+2})} = K_{sp1}\] \hspace{1cm} (4)
or
\[
[Ca^{+2}] [CO_3^{-2}] = Ksp' = \frac{Ksp_{1}}{f_{Ca^{+2}} f_{CO_3^{-2}}}
\]  
(5)

where \(f\) denotes activity coefficients.

\([\text{ ]}\) denotes molar concentrations.

The presence of magnesium ion therefore affects the apparent solubility product of \(CaCO_3\).

Mass action expressions can be written for the remaining reactions; for example, for reaction (8) the equilibrium concentrations of \(Ca^{+2}, SO_4^{-2}\) and \(CaSO_4^0\) are related by the equation:

\[
(Ca^{+2})(SO_4^{-2}) = K_9 [CaSO_4^0]
\]  
(6)

or

\[
\frac{[Ca^{+2}] [SO_4^{-2}]}{[CaSO_4^0]} = K_9 = \frac{K_{9} f_{CaSO_4^0}}{f_{Ca^{+2}} f_{SO_4^{-2}}}
\]  
(7)

Equilibrium constants such as \(K_9\) are functions of temperature, and the activity coefficients are functions of ionic strength and temperature, so that the apparent equilibrium constants such as \(K_{9}'\) for concentrations expressed in molar units are functions of ionic strength and temperature. Equations for the equilibrium constants used in our program are based on those published in References 17 and 18. The activity coefficients for charged species are calculated by an equation based on the Debye-Hückel theory

\[
\log f_i = -\frac{\Lambda Z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I
\]  
(8)

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

\(I = \text{ionic strength} = \frac{1}{2} \sum_i Z_i^2 C_i^2\)

\(Z_i = \text{ionic charge}\)

\(C_i = \text{molar concentration}\)

\(a_i, b_i = \text{parameters calculated from experimental data}\)
The activity coefficients for uncharged species are approximated by equations of the form

$$\log f_i = U_i I$$

where $U_i$ is an empirical constant.

The remaining equations necessary are the equation of electroneutrality and the mass balance equations for calcium, magnesium, carbon and sulfur.

$$0 = [H^+] + [CaHCO_3^+] + [CaCO_3^+] + 2[Ca^{+2}] + [MgOH^+]$$

$$+ [MgHCO_3^+] + 2[Mg^{+2}] - [HCO_3^-] - 2[CO_3^{2-}]$$

$$- 2[SO_4^{2-}] - (OH^-) - R$$

(10)

where $R =$ normality of non-reacting negatively charged species - normality of non-reacting positively charged species, i.e.

$$R = [Cl^-] + [NO_3^-] - [Na^+] - [K^+], \text{ etc.}$$

$$[Ca]_T = [Ca^{+2}] + [CaOH^+] + [CaHCO_3^+] + [CaCO_3^+] + [CaSO_4^{0^-}]$$

$$+ (1-X) [Ca(1-X) MgX CO_3(S)]$$

(11)

$$[Mg]_T = [Mg^{+2}] + [MgOH^+] + [MgHCO_3^+] + [MgCO_3^+] +$$

$$[MgSO_4^{0^-}] + X[Ca_{1-X} MgX CO_3(S)]$$

(12)

$$[C]_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [CaHCO_3^+] + [CaCO_3^+]$$

$$+ [MgHCO_3^+] + [MgCO_3^+] + [Ca_{1-X} MgX CO_3(S)]$$

(13)

$$[S]_T = [SO_4^{2-}] + [CaSO_4^{0^-}] + [MgSO_4^{0^-}]$$

(14)

The 18 chemical species listed earlier are not all independent. For example, when the aqueous phase is saturated in calcium carbonate but not in magnesium hydroxide, then reaction (13) does not apply and the concentration of $CaCO_3^0$ is a dependent variable. We then have 16 independent variables (15 dissolved species, 1 solid species) and 16 independent equations (11 mass action equations, 4 mass balance equations and the electroneutrality equation). In all cases 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 calculating the equilibrium concentrations is described in Appendix A.

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

The results of a sample simulation of a two-stage lime-soda ash softener is shown in Table 1. The raw water composition given in Table 2 is typical of a well water used as cooling tower makeup in an actual coal-fired power plant in the west; the temperature of 20°C is assumed. Solid removal efficiency of 95% is assumed for the settlers. In the first stage reactor, lime and soda ash are added to raise the pH to 10.9 to precipitate Mg(OH)₂ and magnesian calcite. In the second stage reactor, CO₂ is added to reduce the pH to 10.0 and precipitate additional magnesian calcite. The pH in the effluent from the second stage settler is reduced to 7.3 with sulfuric acid to produce stable softened water for makeup to a cooling tower.

The results of a sample simulation of a single-stage sidestream lime-soda ash softener for a cooling tower system is shown in Table 3. The cooling water analysis given in Table 2 is obtained from Reference 12. In the reaction tank, soda ash and lime are added to raise the pH to 9.5. Solid removal efficiency of 95% is again assumed for the settler. The pH in the effluent from the settler is adjusted to 7.8 with sulfuric acid before recycle to the tower. Figure 3 shows the relationship between the pH and the concentration of the lime added, after addition of $7.66 \times 10^{-3}$ moles/l of soda ash. Figure 3 also shows the relationships between pH and several variables.

In Table 4 we compare the results of our computer simulation with those obtained by the bar diagram method for both the well water and the cooling water. Based on the results of several simulations, we conclude that:

1. Total dissolved calcium in the reactor is a minimum at a pH which depends on the influent water composition and temperature; for the cooling water example, the minimum is at pH 9.5. The rate of lime addition can therefore be controlled by feedback from the measured pH.

2. In waters high in sulfate, a large fraction of the total dissolved calcium is in the form of unionized calcium sulfate complex and is unavailable for reaction with carbonate ions.

3. A sharp increase in lime addition is required to raise the pH to precipitate Mg(OH)₂.
TABLE 1. TWO-STAGE SOFTENING OF WELL WATER.

Chemicals added (moles/1) $\begin{array}{l}
\text{Ca(OH)}_2 \quad 7.03 \times 10^{-3} \\
\text{Na}_2\text{CO}_3 \quad 6.18 \times 10^{-3} \\
\text{CO}_2 \quad 6.0 \times 10^{-4} \\
\text{H}_2\text{SO}_4 \quad 2 \times 10^{-4}
\end{array}$

Softening temperature: $20^\circ\text{C}$.

Solids removal efficiency of settlers: 95%.

Composition (in $10^{-3}$ moles/1 unless otherwise noted)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Calcium</td>
<td>6.09</td>
<td>13.12</td>
<td>1.02</td>
<td>1.02</td>
<td>0.23</td>
<td>0.23</td>
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<tr>
<td>Total dissolved Calcium</td>
<td>6.09</td>
<td>0.39</td>
<td>0.39</td>
<td>0.19</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>Total Magnesium</td>
<td>3.34</td>
<td>3.34</td>
<td>0.27</td>
<td>0.27</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Total dissolved Magnesium</td>
<td>3.34</td>
<td>0.11</td>
<td>0.11</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Alkalinity (in $10^{-3}$ equiv/1)</td>
<td>6.40</td>
<td>0.91</td>
<td>0.91</td>
<td>0.81</td>
<td>0.81</td>
<td>0.49</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td>10.9</td>
<td>10.9</td>
<td>10.0</td>
<td>10.0</td>
<td>7.3</td>
</tr>
<tr>
<td>Total dissolved solids (mg/1)</td>
<td>1,820</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Analysis of Well Water and Cooling Water Used in the Computer Simulations

<table>
<thead>
<tr>
<th></th>
<th>Well Water</th>
<th></th>
<th>Cooling Water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/l</td>
<td>mmole/l</td>
<td>mg/l</td>
<td>mmole/l</td>
</tr>
<tr>
<td>Na</td>
<td>167</td>
<td>7.28</td>
<td>15,120</td>
<td>657.4</td>
</tr>
<tr>
<td>K</td>
<td>0</td>
<td>0</td>
<td>240</td>
<td>6.1</td>
</tr>
<tr>
<td>Ca</td>
<td>244</td>
<td>6.09</td>
<td>344</td>
<td>8.6</td>
</tr>
<tr>
<td>Mg</td>
<td>81</td>
<td>3.34</td>
<td>248</td>
<td>10.2</td>
</tr>
<tr>
<td>HCO₃</td>
<td>390</td>
<td>6.40</td>
<td>112</td>
<td>1.8</td>
</tr>
<tr>
<td>Cl</td>
<td>85</td>
<td>2.40</td>
<td>10,064</td>
<td>283.5</td>
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<tr>
<td>NO₃</td>
<td>0</td>
<td>0</td>
<td>30</td>
<td>0.5</td>
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<tr>
<td>SO₄</td>
<td>832</td>
<td>8.65</td>
<td>20,034</td>
<td>208.5</td>
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<tr>
<td>SiO₂</td>
<td>22</td>
<td></td>
<td>39</td>
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<tr>
<td>TDS</td>
<td>1821</td>
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<td>46,231</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td></td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td></td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3. SINGLE-STAGE SOFTENING OF COOLING WATER.

<table>
<thead>
<tr>
<th>Chemicals added (moles/l)</th>
<th>Ca(OH)$_2$</th>
<th>Na$_2$CO$_3$</th>
<th>H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.62 \times 10^{-3}$</td>
<td>$7.66 \times 10^{-3}$</td>
<td>$3.50 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Softening temperature: 40°C

Solid removal efficiency of settler: 95%

<table>
<thead>
<tr>
<th>Composition (in $10^{-3}$ moles/l unless otherwise noted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Total Calcium</td>
</tr>
<tr>
<td>Total dissolved Calcium</td>
</tr>
<tr>
<td>Total Magnesium</td>
</tr>
<tr>
<td>Total dissolved Magnesium</td>
</tr>
<tr>
<td>Alkalinity (in $10^{-3}$ equiv/l)</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Total dissolved solids (mg/l)</td>
</tr>
</tbody>
</table>
Figure 3. Softening of cooling water; lime requirement and concentration of various species vs. pH in the reaction tank.
Table 4. Comparison of Computer Simulation with the Bar Diagram

<table>
<thead>
<tr>
<th>Assumed</th>
<th>Temp. (°C)</th>
<th>Solids Removal (%)</th>
<th>Ca(OH)$_2$</th>
<th>Na$_2$CO$_3$</th>
<th>CO$_2$</th>
<th>Ca</th>
<th>Mg</th>
<th>Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Well Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simulation 1</td>
<td>20</td>
<td>95</td>
<td>7.03</td>
<td>6.18</td>
<td>0.6</td>
<td>0.46</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Simulation 2</td>
<td>20</td>
<td>100</td>
<td>7.03</td>
<td>6.18</td>
<td>0.6</td>
<td>0.63</td>
<td>0.21</td>
<td>0.92</td>
</tr>
<tr>
<td>Bar Diagram</td>
<td>-</td>
<td>100</td>
<td>7.03</td>
<td>6.18</td>
<td>0.6</td>
<td>0.80</td>
<td>0.20</td>
<td>1.00</td>
</tr>
</tbody>
</table>

| Cooling Water          |            |                    |            |               |        |    |    |     |
| Simulation 1           | 40         | 95                 | 1.62       | 7.66          | 0      | 4.67 | 18.96 |     |
| Simulation 2           | 40         | 100                | 0.92       | 7.66          | 0      | 4.57 | 19.27 | 1.80 |
| Simulation 3           | 20         | 100                | 0.92       | 7.66          | 0      | 4.86 | 19.22 | 2.05 |
| Bar Diagram            | -          | 100                | 0.92       | 7.62          | 0      | 0.80 | 20.42 | 0.80 |

* in the settler

** after final settler but before stabilization with CO$_2$ or H$_2$SO$_4$
Field data from lime-soda ash softening of cooling water is available\textsuperscript{6,12,20,21}. We have had varying degrees of success in matching the results of our computer simulations with the field data, since the necessary data input shown in Figure 2 is often not available. We have, therefore, decided to carry out an experimental program to test the computer model.

EXPERIMENTAL RESULTS

Both the National Science Foundation and the Electric Power Research Institute are sponsoring research projects on lime-soda ash softening of cooling water\textsuperscript{22,23}. Softening experiments are to be carried out in small scale models of cooling tower systems.

In our experimental program synthetic waters are softened in the laboratory on a batch basis. The composition and the temperature of the waters are varied systematically to investigate the effects of temperature, ionic strength, magnesium and sulfate on softening performance.

Three experiments have been completed to date. The analyses of the waters are given in Table 5. The experimental procedures for these runs are as follows. Saturated lime solution is added to 1 liter samples of the synthetic water to raise the pH to a pre-determined value. The sample is mixed for 20 minutes. Half of the sample is removed and settled for 20 minutes. The remainder is mixed for an additional 40 min or 100 min and settled. Transfer of $\text{CO}_2$ with the atmosphere is prevented by plastic caps on the vessels. After settling, the supernatant is filtered through glass fibre filters. Before and after filtration the pH and the concentrations of total dissolved calcium and free calcium ion in the supernatant are measured. Total dissolved calcium is determined by EDTA titration and free calcium by ion specific electrode (Orion 93-20).

Experimental results are shown in Figures 4 through 6. Concentrations of calcium in the filtrate and of the lime added are plotted vs. the pH in the filtrate, along with theoretical curves from the computer program. With respect to the concentration of total dissolved calcium, the theory seems to predict accurately the minimum achievable concentration and the pH at which the minimum occurs; at higher pH, however, the theoretical values are consistently below the experimental values. The theory curve for free calcium ion in Experiment 1 does not predict even qualitatively the experimental results. We have no explanations at the moment. In Experiments 1 and 3, there is good agreement between the theoretical lime requirement and the experimental data.

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TABLE 5. ANALYSES OF SYNTHETIC WATERS IN LIME SOFTENING EXPERIMENTS

Concentrations in $10^{-3}$ moles/l.

<table>
<thead>
<tr>
<th></th>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2.5</td>
<td>2.5</td>
<td>1.0</td>
</tr>
<tr>
<td>K</td>
<td>2.0</td>
<td>52.0</td>
<td>52.0</td>
</tr>
<tr>
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<td>2.0</td>
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<td>pH</td>
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<tr>
<td>Temperature (°C)</td>
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Figure 4. Comparison of theory with results of experiment 1.
Figure 5. Comparison of theory with results of experiment 2.
Figure 6. Comparison of theory with results of experiment 3.
The raw waters in Experiments 1 and 2 differ mainly in the concentration of non-reacting background salts, and therefore in the ionic strength. Both the theory and the experimental results show that the increase in ionic strength from Experiment 1 to Experiment 2 is not sufficient to significantly affect the softening performance.

We will be continuing our experimental work with synthetic waters of more complex compositions in the future. If time allows, we will also investigate the removal of silica by softening and the effect of anti-scaling chemicals on softening performance.

REFERENCES


APPENDIX A - CALCULATIONAL PROCEDURES

We assumed that three saturation states are possible:

- 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. The choice of which set of equations to be used is determined in the computer program according to the model of the softening process.

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 apparent equilibrium constants and solubility constants 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 apparent equilibrium and solubility constants 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.