Flue Gas Injection Control of Silica in Cooling Towers

Patrick V. Brady, Susan J. Altman, and Howard L. Anderson, Jr.

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-0754

Abstract

Injection of CO₂-laden flue gas can decrease the potential for silica and calcite scale formation in cooling tower blowdown by lowering solution pH to decrease equilibrium calcite solubility and kinetic rates of silica polymerization. Flue gas injection might best inhibit scale formation in power plant cooling towers that use impaired makeup waters – for example, groundwaters that contain relatively high levels of calcium, alkalinity, and silica. Groundwaters brought to the surface for cooling will degas CO₂ and increase their pH by 1-2 units, possibly precipitating calcite in the process. Recarbonation with flue gas can lower the pHs of these fluids back to roughly their initial pH. Flue gas carbonation probably cannot lower pHs to much below pH 6 because the pHs of impaired waters, once outgassed at the surface, are likely to be relatively alkaline. Silica polymerization to form scale occurs most rapidly at pH ~ 8.3 at 25°C; polymerization is slower at higher and lower pH. pH 7 fluids containing ~220 ppm SiO₂ require > 180 hours equilibration to begin forming scale whereas at pH 8.3 scale formation is complete within 36 hours. Flue gas injection that lowers pHs to ~ 7 should allow substantially higher concentration factors. Periodic cycling to lower recoveries - hence lower silica concentrations – might be required though. Higher concentration factors enabled by flue gas injection should decrease concentrate volumes and disposal costs by roughly half.
ACKNOWLEDGEMENTS

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1. INTRODUCTION

Low-cost methods for controlling calcite and silica scale in power plant cooling waters are needed to allow more efficient utilization of existing water supplies and impaired waters - groundwater, wastewater discharges, produced water from oil and gas operations, and seawater. Power plant cooling towers typically concentrate dissolved solids 3 to 10-fold from feedwater, but in theory might achieve greater water reuse and lower blowdown disposal outlays with more extensive scale prevention. As scaling in cooling towers is often an issues for power plant cooling, independent of utilization of impaired waters, new methods of scale control will provide a general cost-benefit and reduction of water usage.

Silica and hardness (Ca + Mg) removal remain two of the primary cost factors that must be considered when power plants use groundwater and impaired waters for cooling (EPRI 2003). Most groundwaters, and seawater, contain 10 – 100 ppm calcium ion (Ca^{2+}), roughly twice as much bicarbonate (HCO_3^-), and are close to calcite (CaCO_3) saturation. Evaporative concentration increases the likelihood of calcite scale formation, though the actual potential for calcite scaling depends on the ambient P_{CO_2} (or, indirectly, pH) through the reaction:

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-.
\]

The kinetics of calcite growth and dissolution tend to be relatively fast. Calcite solubility decreases with temperature. Calcite scale formation is often controlled with anti-scalants.

Groundwater silica levels range from 10 – 40 ppm. Amorphous silica scale begins to grow when silica levels are concentrated above approximately 120 ppm at 25°C, though the kinetics of the reaction depend critically on pH and other factors as well (see below). High levels of silica supersaturation of roughly twice amorphous silica saturation, can be maintained indefinitely under conditions where polymerization is kinetically inhibited (e.g., Fleming and Crerar, 1982). Silica solubility increases with temperature. Anti-scalants tend to be less effective against silica.

One approach for lowering overall cooling tower water usage is though side-stream nanofiltration (Altman, Cappelle et al. 2010). Continual removal of hardness from cooling tower water with nanofiltration membranes transfers the potential for calcite scale formation to the membranes and the reject fluids. Because > 90% dissolved silica is also rejected by the nanofiltration membranes, the potential for silica scale formation is likewise transferred to the
membrane and reject stream. Limiting calcite and silica scale formation in the process is central to lowering water usage. The primary economic advantage of lowered water use is savings in predicted future rising costs of water and decreased concentrate disposal costs.

The primary disposal method for cooling towers using impaired waters will likely be evaporation ponds or deep well injection. High salt concentrations will probably limit the release of membrane-concentrated blowdown to surface waters or to existing wastewater treatment plants. Decreased water usage through more effective scale prevention would decrease the evaporation disposal outlays (e.g. land purchases, evaporators, crystallizers, etc.) or, in the case of deep well injection, the number of wells needed and pumping costs.

A potentially low cost way to control both silica and calcite scale formation is to use waste power plant flue gas rich in CO₂ to lower pH in the cooling tower waters. A similar approach, but using SO₂ instead of CO₂, is used to prevent silica scaling of geothermal waters (Gallup 1997). Silica polymerization and scale formation can be prevented by lowering pH. Calcite scaling potential likewise decreases with pH (though some calcite scale is often useful for corrosion control).

This report describes 1) theoretical calculations of the potential for scale (both calcium and silica) reduction through lowering pH (Section 2), 2) experiments run to evaluate the time-dependence of silica scale inhibition as a function of pH for concentrated makeup waters (Section 3), and 3) the side effects on cooling tower water stability, and estimate overall cost impacts (Section 4).
2. REDUCTION OF SCALE POTENTIAL OF GROUNDWATERS THROUGH LOWERING pH

Three sources of water were examined to determine the potential pH decrease when equilibrated with approximately 10% CO₂ flue gas: 1) a cooling tower feedwater (CTF) used in a previous SNL-NETL pilot (Mayer et al., 2007), 2) coal bed methane (CBM) produced water from the San Juan Basin, NM, and 3) water chemistries taken from the NatCarb database of impaired ground water from Oklahoma. In other words, these calculations evaluate the acid-neutralizing capacities of these waters. These waters were chosen because produced waters and ground waters are two potential sources of water for cooling. This examination was done by calculating P_{CO₂} of the waters based on measured bicarbonate levels and pH of the water. Once the P_{CO₂} is calculated, an adjusted flue gas equilibrated pH can be calculated using a charge balance calculation. Finally, given the resultant pH and temperature of the waters, it was determined whether calcite and silica will remain dissolved in the water. All calculations are done at 25°C and except where noted, ionic strength effects on aqueous species activity coefficients were neglected.

Table 1 gives the compositions of each of the waters and the calculated P_{CO₂}s and flue gas equilibrated pH. The ambient CO₂ pressure of the CTF water is approximately 10^{-3.2} atm, which is roughly twice that of the atmosphere – 10^{-3.5} atm. Some of this difference might arise from uncertainty in the bicarbonate and pH measurements, and/or slight temperature differences. The higher ambient P_{CO₂} of the CTF water is indicative of its groundwater origins; P_{CO₂} values in groundwater are often 10 to 100 times that of atmospheric levels because of soil respiration in recharge zones and oxidation of organic matter. The CBM water is 10 times saltier than the CTF water and the calculated P_{CO₂} is much higher at approximately 0.12 atm. This might be an overestimate because the bicarbonate level used to estimate it was calculated assuming that all the water alkalinity was bicarbonate ion. The high organic content of the sample would suggest the potential presence of organic acids and, possibly NH₃ groups, which would lead to lower calculated bicarbonate levels. Nevertheless, CBM waters should have P_{CO₂}s higher than atmospheric levels when they are pumped from the ground because higher P_{CO₂}s typically prevail at depth in coal beds.

The groundwater and a CBM produced water were exposed to elevated partial pressures of CO₂ in the subsurface that, once the waters are in contact with the atmosphere, should decrease,
Table 1. Major Element Compositions of SNL Cooling Tower Water, CBM Water, and NatCarb (OK) waters.

<table>
<thead>
<tr>
<th>Ion</th>
<th>aCTF water (ppm) [mol/L]</th>
<th>bCBM water (ppm) [mol/L]</th>
<th>cCBM water, equilibrated (ppm) [mol/L]</th>
<th>NatCarb Range (OK) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>100 [4.3e-3]</td>
<td>4897 [0.213]</td>
<td>4897</td>
<td>0-14,000</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>90.53 [2.6e-3]</td>
<td>2833 [0.08]</td>
<td>2833 [0.08]</td>
<td>43-243,000</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>124.63 [1.3e-3]</td>
<td>2.4 [2.5e-5]</td>
<td>2.4 [2.5e-5]</td>
<td>0-15,000</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>427.39 [7.0e-3]</td>
<td>8048 [0.132]</td>
<td>5436 [0.089]</td>
<td>0-26,000</td>
</tr>
<tr>
<td>F⁻</td>
<td>6.2 [3.2e-4]</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Br⁻</td>
<td>2.7 [3.4e-5]</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Ionic strength (mol/L)</td>
<td>~0.02</td>
<td>~0.2</td>
<td>~0.2</td>
<td>---</td>
</tr>
<tr>
<td>Net charge</td>
<td>-0.0016</td>
<td>0.016</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>pH</td>
<td>8.8</td>
<td>7.6</td>
<td>10.0</td>
<td>4-10.9</td>
</tr>
<tr>
<td>logP_{CO₂} (atm) calculated</td>
<td>-3.2</td>
<td>-0.9</td>
<td>-3.2</td>
<td>---</td>
</tr>
<tr>
<td>Flue gas equilibrated pH</td>
<td>6.7</td>
<td>---</td>
<td>7.9</td>
<td>---</td>
</tr>
</tbody>
</table>

a The SNL cooling tower water composition is taken from Tables 1 and 4 of Interim Report on FWP 08-014250: Nanofiltration Treatment Options for Thermoelectric Power Plant Water Treatment Demands.

b The CBM composition is taken from Table 4.1 of the 2008 Annual Report (New Mexico Small Business Assistance Program Conclusion of Continuation Project, Leveraged) Desalination Technology for Coal Bed Natural Gas Produced Water, Treatment and (1) Rangeland Rehabilitation (2) Riparian Improvement. As the ionic strength is ~ 0.2 mol/L an activity coefficient for HCO₃⁻ of 0.65 is used to calculate \( P_{CO₂} \).

c The pH of the “adjusted” CBM water is calculated assuming a \( P_{CO₂} \) of \( 10^{-3.2} \) atm.
causing a rise in pH. Charge balance calculations suggest that flue gas equilibration will result in pHs near 6 or 7, keeping calcium levels below that where equilibrium calcite formation might occur and pH values below the level where silica polymerization to scale occurs most rapidly.

The pH rise in the CBM water with CO$_2$ outgassing is calculated to be over 2 pH units, from pH 7.6 to 9.9 (see the 3$^{rd}$ and 4$^{th}$ column of Table 1). The calculated pH rise is a maximal value given that there may be other large contributors to the solution alkalinity besides bicarbonate.

The saline groundwaters tabulated in the Oklahoma section of the NatCarb database possess a wide range of compositions. The majority of the subsurface pHs ranged between 6 and 9 and the bulk of the subsurface $P_{CO_2}$ values were calculated to be roughly $10^{-1}$ to $10^{-2.5}$ atm, well above atmospheric levels (with the same caveats noted above). This means that pumping of saline waters for use in cooling towers will prompt CO$_2$ outgassing and pH increases, similar to the CTF and CBM waters; subsequent equilibration with flue gas would lower pH from this baseline.

In summary, these calculations demonstrate that the pH will generally increase when groundwaters (impaired or not) of similar chemsistry examined here are brought to atmospheric pressure. Equilibration with flue gas will lead to a decrease in pH (the amount of which depends on the water chemistry). The extent of the impact this decrease in pH on the solubility of calcium and silica are discussed below and the solubilities of the calcium and silica for the CTF and CBM waters are examined.

**Calcite Scale**

The tendency for calcite to form in cooling tower waters depends on the temperature, pH, dissolved calcium levels, and the ambient partial pressure of CO$_2$. High temperatures, high calcium levels, high pH, and low $P_{CO_2}$ all favor calcite growth. Low temperatures, low calcium levels, pHs, and high $P_{CO_2}$ favor calcite dissolution. Generally increasing $P_{CO_2}$ results in lower pH, and calcite destabilization through the reaction below.

$$2H^+ + CaCO_3 \leftrightarrow CO_2g + Ca^{++} + H_2O$$

Table 2 lists thermodynamic data, taken from the Yucca Mountain Thermodyamic Database data0.ymp.R5d (Yucca Mountain Repository Program 2006), and used the calculations presented
Table 2. Thermodynamic Constants for 25°C Calcite Equilibria.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2, g + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$</td>
<td>-1.47</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$</td>
<td>-6.34</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}^+$</td>
<td>-14.00</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{CaCO}_3 \leftrightarrow \text{HCO}_3^- + \text{Ca}^{++}$</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Figure 1 shows the maximum amount of $\text{Ca}^{++}$ that can be maintained in solution before calcite precipitation occurs as a function of pH and $\text{PCO}_2$ at 25°C.

The “calcite-saturated solution” line in Figure 1 denotes the pH of a CaCO$_3$-H$_2$O equilibrated solution and illustrates the general trend of fluid pH with increasing $\text{PCO}_2$. Each order of magnitude increase in $\text{PCO}_2$ results in a pH decrease of roughly 0.7 units causing the saturated Ca$^{2+}$ level to roughly double. Figure 1 also shows that the CBM water is approximately at

![Figure 1. Calculated equilibrium solubilities of calcite as a function of pH and temperature (top) and as a function of pH and $\text{PCO}_2$ at 25°C (bottom). The connected, shaded dots define a right-to-left trajectory of the calculated pH and Ca$^{++}$ levels in a saturated calcite-H$_2$O system with increasing $\text{PCO}_2$.](image-url)
equilibrium with calcite at 25°C. The CTF water is oversaturated with calcite. Degassing of the CBM water from its \textit{in-situ} value of 0.12 atm to lower values would shift it to higher pH and result in calcite scale formation.

A key assumption in the above calculation is that there are no kinetic obstacles to equilibration of CO$_2$ with the cooling tower fluid and that there is enough flue gas to saturate the fluid. Therefore the calculated pH decreases are maximum values. Both factors depend on the ultimate design of the CO$_2$ injector.

In summary, recarbonation with flue gas can lower the pHs of these fluids back to roughly their initial pH, though the potential for calcite precipitation will be substantially less if calcite precipitation removes a portion of the Ca$^{++}$ from the fluid before introduction into the cooling tower (the process might be hastened by seeding). Flue gas carbonation probably cannot lower pHs to much below pH 6 because the pHs of impaired waters, once outgassed at the surface, are likely to be relatively alkaline.

**Silica Scale**

The mechanism of amorphous silica scale inhibition by flue gas injection is fundamentally different from that of calcite scale inhibition; lower pHs slow the kinetics of silica polymerization to scale, as opposed to shifting the equilibria controlling calcite formation. Increasing pH above pH 9 decreases both the silica polymerization rate and the equilibrium solubility of silica (Figure 2). Raising temperature also raises silica solubility (Figure 2 and 3) and works against silica scale formation.

Although dissolved silica levels at 25°C should not exceed amorphous silica saturation, approximately 120 ppm at pH 7, much higher levels can remain stable if silica polymerization to amorphous silica is kinetically inhibited by, for example lowering the pH below 6 or above 9 (Rothbaum, Anderton et al. 1979; Gallup 2002). When solutions become saturated with amorphous silica, silica monomers in solution begin to polymerize after an induction period which can be extensive. Figure 4 shows how the induction period for silica scale formation from NaCl solutions depends on pH and is longest at sub-neutral, acidic pHs.
Figure 2. Amorphous silica solubility from pH 4-10, 25-200°C, calculated from the regression of Fournier and Rowe (Fournier and Rowe 1977) and the silicic acid constants tabulated in data0.ymp.R5d (Yucca Mountain Repository Program 2006).

Figure 3. Neutral pH temperature-dependent quartz and amorphous silica solubilities calculated from the regression of Fournier and Rowe (1977)
Figure 4. Silica polymerization kinetics as a function of pH. From Gunnarsson and Arnorsson (2005). “Molybdate active silica” = silica monomers.

Silica polymerization rates in more complex cooling tower solutions cannot be predicted, but instead must be measured.
3. EXPERIMENTAL EVALUATION OF SILICA SCALE REDUCTION

The experimental proxy for impaired water that we examined is cooling tower blowdown from Sandia National Laboratories Building 518 or the Center for Integrated Nanotechnology (CINT). This cooling tower is used to cool a building with both laboratory and office space. The blowdown is evaporatively concentrated groundwater. This cooling tower is currently being used to evaluate the effectiveness of nanofiltration to reduce water usage in cooling towers. Table 3 gives the major element composition of CINT cooling tower blowdown. Equilibration of the CINT blowdown with 10% CO\textsubscript{2} flue gas is calculated to lower the pH to 6.6.

The following steps were taken to five separate volumes CINT blowdown:

1. water was acidified to pH ~ 5 (5.1) to prevent polymerization,
2. water was evaporated to half its volume to increase the silica concentrations,
3. water was cooled to 25\textdegree C,
4. pHs of water were adjusted by adding NaOH, and
5. monomeric silica concentrations were monitored in the solutions over time.

Four solutions were adjusted upwards to pHs of 6, 7.1, 8.2, and 9.1; the pH 5.1 solution was used as is. pH was measured using an electrode standardized at pH 4 and 10. Monomeric silica was measured using the HACH Silica test which relies on the molybdate blue reaction.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (ppm) [mol/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsuperscript{+}</td>
<td>152 [6.6e-3]</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+}</td>
<td>163 [4.1e-3]</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>27 [1.1e-3]</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>105 [3.0e-3]</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>139 [1.4e-3]</td>
</tr>
<tr>
<td>HCO\textsubscript{3}\textsuperscript{-}</td>
<td>374 [6.1e-3]</td>
</tr>
<tr>
<td>K\textsuperscript{+}</td>
<td>25 [6.3e-4]</td>
</tr>
<tr>
<td>SiO\textsubscript{2,aq}</td>
<td>109 [1.8e-3]</td>
</tr>
<tr>
<td>pH</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 3. Major element composition of CINT cooling tower blowdown.
Because of the pre-evaporation before the beginning of the experiments, silica monomer concentrations (and that of the other conservative ions) were twice the levels in Table 3 (approximately 220 ppm). Amorphous silica saturation at this temperature and these pHs is approximately 120 ppm (Figure 2), which means that the starting solutions were over-saturated with respect to amorphous silica and thermodynamically favored to polymerize and form scale. Polymerization and scale formation would be indicated by a decrease in monomeric silica concentration in solution over time.

Figures 5 and 6 show measured pH-dependent silica polymerization formation. Note that appreciable scale formation is confined to the pH 8 run. Lowering the pH of the CINT Cooling Tower Water apparently inhibits the kinetics of silica scale formation for several dozen hours over which these experiments were run. Flue gas injection of CO₂ should be able to shift the pH of cooling tower waters to roughly pH 7. The results in Figure 6 indicate that this pH shift should prevent silica scale formation for > 180 hours, and confirms the feasibility of flue gas injection for silica scale control for this particular water. Because the observed inhibition is consistent with previous researchers observations and the composition of the CINT water is a reasonable proxy for concentrated groundwaters suggests that flue gas injection might be widely applied. Confirmatory experiments would have to be done before actual implementation at power plant sites.

Figure 6 suggests that the lag time for silica scale nucleation and growth at pH 7 is roughly two weeks (which is equal to 336 hours). Because the pH effect on silica control is temporary, the membranes would have to be periodically run at lower recoveries, or the flow reversed (see e.g. Gilron, Waisman et al. 2006). The process works at the molecular level by the following steps: 1. Lowered pH slows the formation of silica scale nuclei, and 2. Flow reversal removes nascent scale nuclei immediately before they are able to enter their fast growth phase. The net effect is to maintain silica levels during nanofiltration that are roughly twice the saturated value for amorphous silica.
Figure 5. Silica scale formation from evaporatively concentrated CINT water.

Figure 6. pH-dependence of silica scale formation from evaporatively concentrated CINT water.
4. COST ANALYSIS

The flue gas injection approach outlined above might lower nanofiltration cooling tower water treatment costs by: 1. Decreasing the amount of nanofiltration reject water (concentrate) to be disposed of by allowing higher concentration factors; and 2. Possibly substituting no-cost flue gas CO₂ for sulfuric acid in pre-treatment to lower warm-lime softening (or other silica removal) costs. We focus here on the cost implications of the decreased reject volume. Cost comparison of the chemical treatment outlays will follow in a subsequent report that focuses on zero liquid discharge disposal of blowdown. Flue gas injection of CO₂ appears capable of roughly doubling the amount of silica in the concentrate stream, which corresponds to a net decrease of roughly half the concentrate volume to be disposed. In inland areas where impaired waters are most likely to be utilized, the concentrate will be injected into deep wells or evaporated in ponds possibly using evaporators and crystallizers. Again, discharge to wastewater treatment plants is assumed to be unlikely because of the salt load in the concentrate. Preliminary cost analysis of the nanofiltration approach (Altman, Cappelle et al. 2010) considered a plant producing 8,000 m³/day (or 1,500 gpm) of blowdown. Nanofiltration in the absence of flue gas injection was calculated to reduce this volume by 30-75%, the limiting factor being the potential for silica scale formation with further concentration. For the purposes of estimating costs, we set the baseline nanofiltration concentrate discharge to 4000 m³/day (50% reduction) and the flue gas injection nanofiltration concentrate discharge to 2000 m³/day (375 gpm), because flue gas injection silica levels are maintained at roughly twice that of the base case.

EPRI (2003) estimated the costs of cooling tower discharge to evaporation ponds in the Central Valley of California equipped with evaporators + pond and evaporators & crystallizers. For 194 gpm (279360 gpd) concentrate discharge from a plant using produced water, disposal costs (amortization + operating) were estimated at 5,205 $/day (evaporators + pond) and 4,612 $/day (evaporators & crystallizers) which correspond to respectively 0.0186 $/gal and 0.0165 $/gal assuming costs scale linearly to volume of concentrate treated. This would suggest that costs for concentrate disposal with an evaporator and pond for the nanofiltration case of Altman et al. (2010) would be lowered by half, from 7.4 M$/yr to 3.7 M$/yr. This neglects the one-time cost of engineering the diversion of flue gas into the cooling tower reservoir.

Note that even lower pHs, and substantially lower polymerization rates, might be achieved by introducing SO₂ from pre-scrubbed flue gas to form sulfurous acid (H₂SO₃). Using sulfurous
acid (H$_2$SO$_3$) as a silica scale inhibitor has many advantages, for example: 1. H$_2$SO$_3$ is less acidic and therefore less corrosive than sulfuric acid; 2. It can scavenge oxygen to prevent pitting corrosion; 3. Bisulfite complexes with silica monomers decreasing the thermodynamic driving force for silica scale formation (Gallup 1997). Alternatively, raising pHs to above 9.5 by, for example, adding alkali from fly ash leaching, might prevent silica scale formation by raising the solubility of silica and by slowing the kinetics of polymerization. However, these higher pH’s would increase the impact of calcium scaling.
5. REFERENCES


Yucca Mountain Repository Program (2006). Thermodynamic Data Base data0.ymp.R5d.
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External (Electronic Copy)

I. Andy Aurelio
National Energy Technology Laboratory
Morgantown, WV
Isaac.Aurelio@netl.doe.gov

Lynn Brickett
National Energy Technology Laboratory
Pittsburgh, PA
Lynn.brickett@netl.doe.gov

Jared Ciferno
National Energy Technology Laboratory
Pittsburgh, PA
Jared.Ciferno@netl.doe.gov