

Steam Generator Management Program: Laboratory Testing to Validate pH and Conductivity MULTEQ Calculations, Revision 1



2011 TECHNICAL REPORT



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Steam Generator Management Program: Laboratory Testing to Validate pH and Conductivity MULTEQ Calculations, Revision 1

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PRODUCT DESCRIPTION

Measures to control corrosion processes in steam generators have for the most part proven successful to date, but intergranular attack/stress corrosion cracking (IGA/SCC) of Alloy 600 continues to occur in steam generators at some nuclear plants. The present mitigation strategy is based on the premise that crack initiation and propagation rates depend on pH and electrochemical potential. There is some evidence suggesting that lead (Pb) may play a key role.

This report documents laboratory testing to validate MULTEQ calculations of at-temperature pH and obtain high-temperature conductivity information. MULTEQ is a widely used tool that provides an estimation of local water chemistry conditions in flow-restricted regions. The research described in this report is geared toward enhancing MULTEQ's usefulness for predicting conditions that can cause IGA/SCC and for identifying corrective actions.

Results and Findings

Commercial cells that measure the conductivity of solutions above 100°C are not available. Phase 1 of this research therefore designed and constructed a cell for measuring conductivities of solutions up to 280°C. In Phase 2, the pH and conductivity of ten different test solutions were measured as they were heated from room temperature to 280°C and as they cooled down. Analysis of the results was performed to validate MULTEQ calculations and the accuracy of the MULTEQ database. The study provided valuable input for potential future database additions or possible software revisions to increase the validity of predictions.

Challenges and Objectives

The objective of this work was to validate the MULTEQ pH and conductivity calculations. This will in turn enable the tool to provide plant operators with an improved understanding of plant operating conditions that produce local chemistries conducive to SCC, particularly cracking conditions in which Pb plays a role (PbSCC).

Applications, Value, and Use

An improved understanding of the accuracy of MULTEQ calculations gained from this work will support the following:

- More accurate definition of plant operating conditions to prevent SCC, particularly PbSCC
- A better understanding of approaches needed for developing remedial action for PbSCC
- Increased reliability of steam generators
- Input to the MULTEQ Database Committee for possible database revisions and additions

Approach

Test solutions were established containing species found in the secondary water of nuclear steam generators. These solutions consisted of three single-component solutions, a magnetite buffering solution, and two sets of crevice simulation solutions—one set with Pb and one set without Pb. The crevice simulation solutions were adjusted to MULTEQ-calculated low, medium, and high pHs. The conductivity of the test solutions was measured every 25°C between room temperature and 280°C. The at-temperature pH was measured every 25°C from 175°C to 280°C.

Keywords

Steam generator

MULTEQ

PbSCC

Conductivity

High-temperature pH

ChemWorks tools

ABSTRACT

Intergranular attack/stress corrosion cracking (IGA/SCC) of Alloy 600MA steam generator tubes continues to be an issue in the tube/tube support plate crevices and top of tubesheet locations in recirculating steam generators. An important tool in predicting conditions that can cause IGA/SCC and in identifying corrective actions is the MULTEQ software code, which performs calculations of local chemistries in flow-restricted regions.

The present strategy for mitigating IGA/SCC is based on the premise that crack initiation and propagation rates depend on pH and electrochemical potential. Validating the MULTEQ-calculated at-temperature pH and obtaining high-temperature conductivity information, as addressed in the research described in this report, therefore enhances the code's usefulness to plants as they address this particular water chemistry-related issue.

This report describes laboratory investigations performed to determine the pH and conductivity of test solutions developed by MULTEQ calculations. These solutions consisted of species found in secondary water of nuclear steam generators. There were ten test solutions: three single-component salt solutions, two sets of crevice simulation solutions with and without lead, and a magnetite buffer solution. The crevice simulation solutions were adjusted to MULTEQ-calculated low, medium, and high pH.

The conductivity of the test solutions was measured as they were heated to 280°C and as they cooled down. The conductivity results for the single component NaCl and Na₂SO₄ solutions were in accordance with MULTEQ speciation predictions. The conductivity results for the single component CaCl₂ solution suggest that the diamer, CaCl⁺, may need to be added to the MULTEQ code.

The pH of the test solutions was measured between 175°C and 280°C. With the exception of the two highly acidic solutions, the measured pH values were in good agreement with MULTEQ predictions at 280°C, and within one pH unit at 250°C. The pHs of the two highly acidic solutions were significantly higher than the MULTEQ predictions, suggesting that system materials were corroding. At lower temperatures, the agreement between measured and MULTEQ values was not as good. A comparison of the conductivity measurements during heat-up and cool-down suggest that this lack of agreement could be because equilibrium conditions did not exist when the pH measurements were made. The MULTEQ code contains thermodynamically stable forms of the various precipitates and does not consider the formation of more soluble intermediates, which are known to exist.

The results for the magnetite buffer solution support the hypothesis that extremely low pH is not likely to occur in operating steam generator crevices, because of magnetite dissolution.

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1

INTRODUCTION

Fundamental principles of corrosion science suggest that maintaining low impurity concentrations, low levels of oxygen and moderately alkaline pH will minimize corrosion in steam generators. Thus, measures have been implemented to increase the secondary water purity and to reduce oxygen ingress. Plants have implemented an all volatile treatment (AVT), typically involving the addition of hydrazine, to maintain reducing conditions, and amines for pH control. Some plants have also added boric acid or titanium oxide to attempt to minimize corrosion. These measures were generally successful in controlling denting and pitting by the early 1990s. However, they have not prevented IGA/SCC of Alloy 600, although laboratory data suggest that crack initiation and propagation rates are negligible in mildly alkaline with reducing conditions at steam generator temperatures. Tube damage by IGA/SCC continues in some plants, and not in others. Although, the reason for the variability is not known, there is a growing collection of data that suggest that lead (Pb) is responsible [1-11].

An important element in predicting conditions, which can cause lead assisted stress corrosion cracking (PbSCC), and in identifying corrective actions, will be accurate calculations of crevice and other local chemistries. MULTEQ is an EPRI code which provides estimations of the chemical conditions in flow restricted regions in steam generators and other operating plant systems. However, these estimations are based on specific speciation models and may not contain all the relevant species for specific situations. As an example, lead potentially forms many soluble as well as insoluble species in steam generator secondary water chemistries. The MULTEQ calculations contain the hydrolysis products, the chloride complexes, and the oxide, phosphate, and several silicates as precipitates. Other possible species have not yet been included in the database. In addition, concentrated electrolyte solutions are non-ideal and difficult to characterize chemically as well as thermodynamically. Conductivity measurements provide a means for evaluating the performance of activity models and of obtaining association constants. Validating the MULTEQ calculated at-temperature pH (pH_T) and obtaining high temperature conductivity information is addressed in this program.

2

EXPERIMENTAL PROCEDURES

Electrochemical measurements were performed in an Alloy 718 autoclave designed and constructed at Teledyne Scientific. The body of the two liter autoclave was sealed at both ends. It was operated in a horizontal position. The lid on one end had five symmetrically spaced ports for commercial Conex fittings to accommodate 3.2 mm diameter Ni feedthrough rods. A high pressure gas introduction line with a safety pressure relief valve was welded into the center of the lid. The other lid had two ports for Conex fittings used for attaching a reference electrode and a pH electrode. The autoclave was surrounded by a thermally insulated electric heating blanket with an electronic proportional-integral-differential (PID) temperature controller.

An external Ag/AgCl, pressure balanced, high temperature reference electrode was assembled using a design that was a modification of designs published previously [12, 13]. This was constructed using a 10 cm long, 3 mm O.D., 0.8 mm wall Ti tubing to form the support for the active Ag/AgCl portion of the reference electrode. The reference compartment of the electrode contained a silver-plated 5 cm Ti rod. The plated Ag was chloridized anodically in 1 M HCl by passing 2 mV/cm² for two hours. The Ag plated Ti rod was then inserted into a 60 cm long heat shrink tetrafluoroethylene (TFE) tube with approximately 2.5 cm protruding outside of the tube. The TFE/Ag/AgCl assembly was sealed in a Conex, ceramic insulated pressure fitting. A Swagelok fitting was attached to the other end of the Ag/AgCl coated Ti rod. The TFE tube was filled with ZrO powder and the end was sealed with a porous zirconia plug, 3 mm by 1.3 cm long. A reservoir of 0.1 M KCl was attached to the Swagelok fitting on the Ti rod, and solution was allowed to flow into and saturate the ZrO powder, forming a salt bridge between the Ag/AgCl and the porous zirconia plug. The reference electrode was checked for continuity and the potential was compared to a standard calomel reference electrode at room temperature (SCE). The potential difference was approximately 44 mV. The electrode was completed by attaching the Conex fitting into a copper tubing wrapped, stainless steel tube water jacketed for cooling the external compartment of the reference electrode assembly. A schematic and photograph of reference electrode are shown in Figure 2-1.

The pH measurements were made using a yttria-stabilized zirconia pH sensor with an internal Cu/Cu₂O couple [14]. The assembly was obtained from Corr Instruments. A photograph of the pH electrode is shown in Figure 2-2. The operation of the pH electrode depends upon the yttria-stabilized membrane performing as an efficient conductor of oxygen ions at the operating temperature. The hydrogen ion activity (pH) on the liquid/ceramic interface affects the oxygen vacancy concentration of the ceramic and further the Cu/Cu₂O electrode. The pH_T is calculated using the Nerst relationship:

Experimental Procedures

$$pH_T = [E^{\circ}_{Cu/Cu_2O} - (E_{Ag/AgCl}(pH) + A)] / 2.303 RT$$

Where E°_{Cu/Cu_2O} = Standard equilibrium potential of Cu/Cu₂O

$E_{Ag/AgCl}(pH)$ = Electrode potential of the pH electrode

A = Correlation constant at T to convert the $E_{Ag/AgCl}$ potential to SHE

R = Gas constant

T = Temperature (Kelvin)

The values of the standard equilibrium potential of Cu/Cu₂O for the test temperatures were obtained from Macdonald [15].

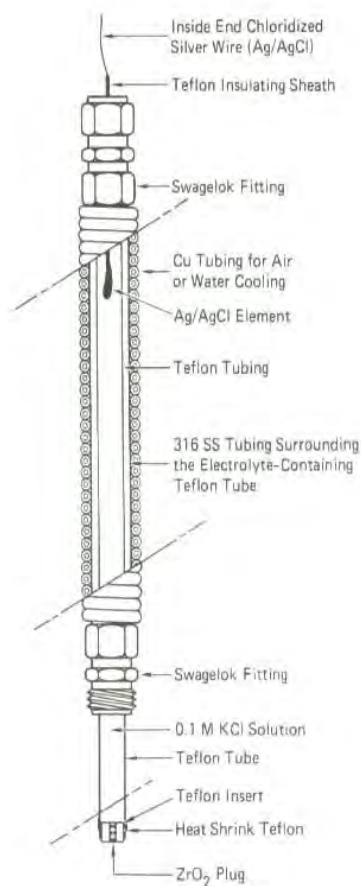


Figure 2-1
Schematic and Photograph of External Pressure Balanced Ag/AgCl Reference Electrode.



Figure 2-2
Photograph of yttria-stabilized Zirconia pH Sensor

Conductivity measurements in plants are made with commercial devices operating at room temperature. This program requires a device that can be used up to 280°C. In Phase 1 of this program a high temperature conductivity cell was designed and constructed [16]. It consists of two Pt sheets mounted on zirconia plates. These are held in place by zirconia tube spacers mounted on Alloy 600 screws. Pt leads are spot welded to each plate. Electrical conductivity of a solution is obtained by measuring the resistance of the solution from AC impedance measurements across the two parallel platinum plates using the following equation.

$$\sigma = 1/\rho = L/AR$$

Where σ = Conductivity of solution

ρ = Resistivity of solution

L = Separation of plates

A = Cross sectional area of plates

R = Resistance of solution

The quantity L/A is called the cell constant (k), which is obtained experimentally by using solutions of known conductivity at different temperatures. For accurate measurements, the dimensions of the cell must remain constant with temperature. Photographs of the cell are shown in Figure 2-3.



Figure 2-3
Views of Conductivity Cell Used in High Temperature Solutions

The solution resistance is measured by taking a frequency scan of the AC impedance of the cell. In general, the impedance data is interpreted by constructing an equivalent circuit with circuit elements that represent the physical processes taking place. For example, the equivalent circuit for a corroding electrode is shown in Figure 2-4. The resistance, R_{ct} , is the charge transfer resistance associated with the current of positive ions moving from the metal surface into solution. The capacitance, C_{dl} , is the double layer capacitance produced by the negative surface charge on the metal and the sheet of positive ions in solution adjacent to the metal surface. Finally, the R_s is the solution resistance.

Figure 2-5 shows the frequency scan of the AC impedance and the corresponding phase angle between the current and potential for an ideal system. Looking at the limits, in the dc limit the impedance is the sum of the charge transfer resistance and the solution resistance and the phase angle is zero. In the high frequency limit the impedance is the solution resistance with a zero phase angle. Between these frequency limits the impedance is dominated by the double layer capacitance and has a $1/f$ dependence with a 90° phase angle.

The impedance of the conductivity cell was measured using a Gamry Framework Impedance System. Frequency scans were made from 0.01 Hz to 10^6 Hz. The solution resistance, R_s , was taken as the value of the impedance where the phase angle was zero in the high frequency limit.

Experimental Procedures

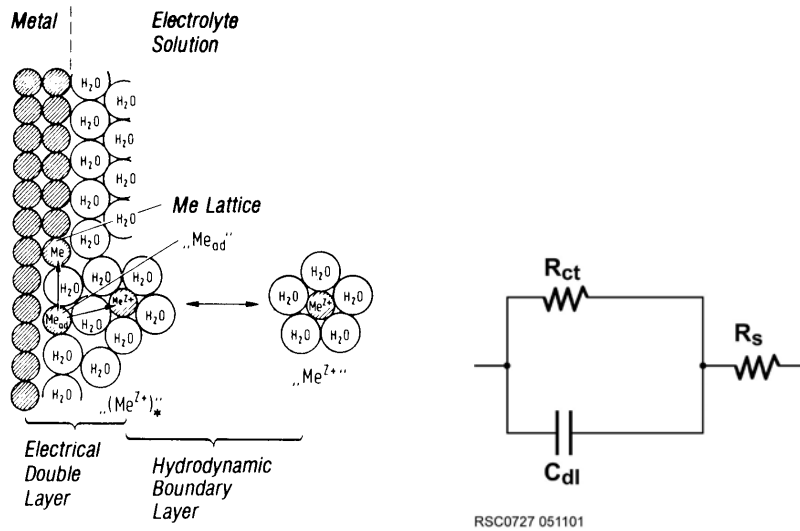


Figure 2-4
Schematic of Physical Processes Occurring on a Corroding Metal Surface and Equivalent Circuit That Represent These Processes

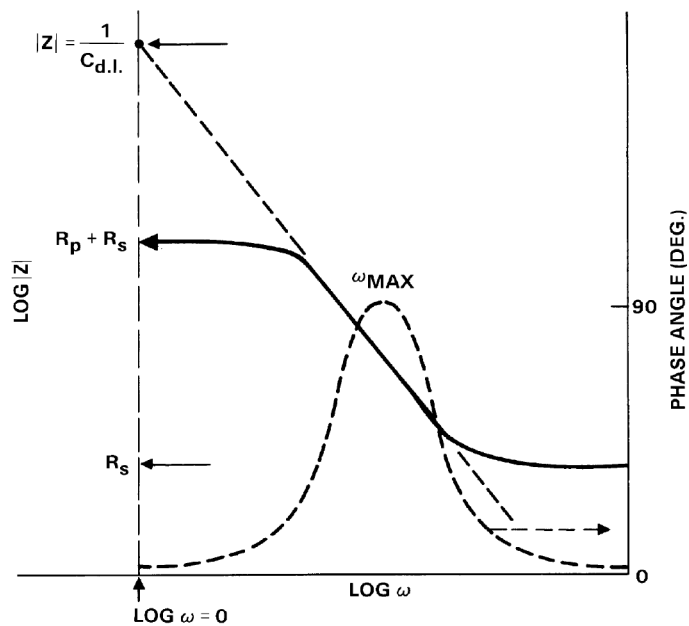


Figure 2-5
Schematic Showing the Frequency Dependence of AC Impedance, and Phase Angle

Figure 2-6 shows the autoclave with the attached electrodes and conductivity cell. Figure 2-7 shows the autoclave surrounded by the thermal blanket and seated in the bottom section of the Al “blast shield” with the Ag/AgCl reference electrode to the right and the pH electrode to the left. The gas introduction and return lines are located above the autoclave.



Figure 2-6
Autoclave Immediately After Sealing with Test Solution



Figure 2-7
Autoclave Enclosed in Thermal Blanket and Seated in Bottom Section of Clam Shell Blast Shield

Experimental Procedures

The rationale for the development of the test solutions is discussed in Appendix A. These solutions contained species found in the secondary water of nuclear steam generators and consisted of three single component solutions, a magnetite buffering solution, and two sets of crevice simulation solutions, one set with and one set without Pb. The crevice simulation solutions were adjusted to MULTEQ calculated low, medium, and high pHs.

Test solutions makeup compositions were:

1. 1.5 m NaCl(s)
2. 1.5 m CaCl₂(s)
3. 1.5 m Na₂SO₄(s)
4. Crevice Simulation 1-Low pH: 1.5 m NaCl(s) + 0.25 m Na₂SO₄(s) + 0.3 m SiO₂(s) + 0.075 m Al₂O₃(s) + 0.00333 m Fe₃O₄(s) + 0.0318 m PbO(s)
5. Crevice Simulation 1-Medium pH: Same composition as item 4 above but with the addition of 0.12 m KOH(s)
6. Crevice Simulation 1-Hhigh pH: Same composition as item 4 above but with the addition of 0.50 m KOH(s)
7. Crevice Simulation 2-Medium pH: 0.3 m NaCl(s) + 0.15 m Na₂SO₄(s) + 0.15 m CaCl₂(s) + 0.05 m KCl(s)
8. Crevice Simulation 2-High pH: Same as item 7 above but with the addition of 0.40 m NaOH(s)
9. Crevice Simulation 2-Low pH: Same as item 7 above but with the addition of 0.05 m NaHSO₄(s)
10. Magnetite buffering solution: 1.5 m NaCl(s) + 0.02 m HCl + 0.0333 m Fe₃O₄(s)

The solutions were prepared by adding a calculated volume of DI water to a beaker. Then the calculated weights of components that are soluble at room temperature were added and stirred until they dissolved. Weighed-out powders of oxides and salts that were not completely soluble at room temperature were first placed in the autoclave before adding the solution containing the room temperature soluble species.

The cover gas was 5% hydrogen/95% argon. Before heating, the solution was deoxygenated in the autoclave by three pressurizing/aspirating cycles from 1.4 MPa to 13.6 MPa (200 psia to 2000 psia). Each pressurization was held for 30 minutes followed by a slow release of the gas. No hydrazine was added for oxygen removal. Following the last aspiration, heating was begun with a 1.4 MPa (200 psia) overpressure to maintain a stable immersion level. The autoclave heaters were then activated. The conductivity of the test solutions were measured every 25°C between room temperature and 280°C. The at-temperature pH was measured every 25°C from 175°C to 280°C.

3

RESULT AND DISCUSSION

The conductivity cell was constructed with dimensions to have a cell constant of approximately 1.0. The actual cell constant was determined using standard solutions of known conductivity. This was checked using a room temperature commercial conductivity meter (Corning 441), which gave results indicating a cell constant of 0.98. This calibration was also validated by comparing conductivities determined from impedance measurements with literature values of 0.4 m NaCl up to 250°C [17] as shown in Table 3-1.

Table 3-1
Comparison of Conductivity of 0.4 m NaCl Measured Using the Teledyne Cell with Literature Values [17]

Temperature, °C	Conductivity, mS/cm (Huang)	Conductivity, mS/cm (Teledyne)
25	37	37
50	58	64
75	80	84
100	100	100
125	118	117
150	134	132
175	148	154
200	159	161
225	168	150
250	176	170

After validating the cell constant in the temperature range of interest, the conductivity of the test solutions, with the exception of Crevice Simulation 1-Medium pH, were determined. Conductivities were determined from impedance measurements made as the temperature of the autoclave increased from room temperature to 280°C. The temperature increased at a rate of approximately 25°C every 30 minutes. The autoclave was maintained at 280°C for one hour, and then the heaters were switched off. Measurements were made again as the autoclave cooled down. The conductivity values are shown in Tables 3-2 through 3-10.

Result and Discussion

Table 3-2
Effects of Temperature on Conductivity of 1.5 m Na₂SO₄

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	139	139
50	219	
75	224	
100	329	
125	350	337
150	374	366
175	408	391
200	418	400
225	400	408
250	374	366
280	353	353

Table 3-3
Effects of Temperature on Conductivity of 1.5 m CaCl₂

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	127	
50	374	
75	322	
100	374	
125	392	391
150	417	436
175	436	455
200	444	392
225	454	392
250	454	374
280	425	420

Table 3-4
Effects of Temperature on Conductivity of 1.5 m NaCl

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	125	
50	202	
75	237	
100	284	
125	310	
150	316	315
175	338	338
200	352	352
225	375	358
250	383	367
280	392	387

Table 3-5
Effects of Temperature on Conductivity of Crevice Simulation 1 – Low pH

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	93	
50	160	
75	189	
100	204	218
125	228	
150	247	291
175	259	314
200	279	334
225	268	338
250	282	337
280	311	312

Result and Discussion

Table 3-6
Effects of Temperature on Conductivity of Crevice Simulation 1 - High pH

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	152	94
50	305	
75	359	
100	397	196
125	432	227
150	446	255
175	446	275
200	413	297
225	387	325
250	352	338
280	326	326

Table 3-7
Effects of Temperature on Conductivity of Crevice Simulation 2 - Low pH

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	39	
50	67	
75	111	
100	128	
125	151	148
150	164	161
175	173	174
200	187	187
225	186	196
250	182	195
280	186	187

Table 3-8
Effects of Temperature on Conductivity of Crevice Simulation 2 - Medium pH

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	27	76
50	24	
75	94	
100	111	173
125	133	199
150	158	222
175	179	238
200	199	254
225	254	263
250	263	268
280	266	268

Table 3-9
Effects of Temperature on Conductivity of Crevice Simulation 2 - High pH

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	101	103
50	183	
75	222	
100	244	
125	263	253
150	277	275
175	293	293
200	305	304
225	312	305
250	308	302
280	297	296

Table 3-10
Effects of Temperature on Conductivity of Magnetite Buffering Solution

Temperature, °C	Conductivity, mS/cm (temperature increasing)	Conductivity, mS/cm (temperature decreasing)
25	104	118
50	149	
75	180	229
100	209	259
125	233	293
150	252	319
175	319	333
200	359	358
225	374	383
250	399	383
280	400	403

Figures 3-1, 3-2, and 3-3 are semi-log plots of the conductivities during heat-up as a function of temperature. The conductivities are grouped as follows: Figure 3-1 shows the single component solutions, Figure 3-2 shows the Crevice Simulation 1 solutions with the conductivity curves of Na_2SO_4 and the Magnetite Buffer solution (sodium sulfate and magnetite are components of Crevice Simulation 1 solutions), and Figure 3-3 shows Crevice Simulation 2 solutions with the conductivity plots of sodium sulfate and calcium chloride, which are components of Crevice Simulation 2 solutions.

Figure 3-1 shows that the conductivity of NaCl increased monotonically with temperature during the heat up stage. As predicted by MULTEQ [18], this behavior occurs because Na^+ and Cl^- are totally soluble over the entire temperature range. The Na^+ and Cl^- ions have no tendency to form associated species at these temperatures and this concentration. Thus, the equivalent conductance of the ions increases with temperature.

In contrast, the conductivities of Na_2SO_4 and CaCl_2 reach a maximum at 200°C and 225°C, respectively. This behavior has been observed previously for sulfates [17] and indicates the onset of the formation of species with lower electrical conductance. Figure 3-4 shows the MULTEQ predicted speciation for 1.5 m Na_2SO_4 in the temperature range investigated. All the 1.5 m $\text{Na}_2\text{SO}_4(\text{s})$ added to the autoclave is not soluble until the temperature increases above 150°C. MULTEQ also predicts that the neutral $\text{Na}_2\text{SO}_4(\text{aq})$ specie increases with temperature with Na^+ and SO_4^{2-} decreasing with temperature. However, the equivalent conductance of all the ionized species increases with temperature and offsets the decrease in ionic species concentrations to some extent. Figure 3-5 shows a plot of the total ion concentration in solution and the measured

conductivities for this solution. The two parameters show very similar trends although the measured conductivity maximum is offset to higher temperatures. This offset is possibly a result of a lag time in reaching equilibrium within the autoclave in combination with the increasing equivalent conductancies. Mixing within the autoclave is by diffusion and thermally generated currents induced by the autoclave heating. So equilibrium concentrations throughout the entire autoclave may not be totally achieved at each temperature as some of the products are not totally dissolved.

The calcium chloride solution decreases in conductivity above 250°C was much smaller than that observed for sodium sulfate and was not repeated during the cooldown. MULTEQ predicts that all the $\text{CaCl}_2(\text{s})$ should be soluble over the entire temperature range and only contains one combination specie CaOH^+ . At the low predicted pH_T of 4.4, this combination specie is not significant. Another code predicts that the CaCl^+ diamer would be a significant specie at the test conditions and its formation increases with increasing temperature. The MULTEQ Database Committee may want to consider evaluating whether addition of this specie to the database would be beneficial. At lower temperatures the conductivities of Na_2SO_4 and CaCl_2 are greater than that of NaCl as a result of the higher ionic strength of these solutions since the total Na^+ is higher for the Na_2SO_4 solution and the total Cl^- is higher for the CaCl_2 solution.

Figure 3-2 gives the temperature dependence of the conductivity of the Low and High pH Crevice Simulation 1 solutions compared to those of the Magnetite buffer and sodium sulfate solutions. The latter two species are components of the three Crevice Simulation 1 solutions. The Low pH Crevice Simulation 1 solution is the only solution other than NaCl that does not have a maximum or plateau in the conductivity-temperature curve. However, the conductivity of this Crevice Simulation solution is lower than that of 1.5 m NaCl although it also contains 1.5 m NaCl . However, as shown in Table 3-5, conductivities were higher during the cooldown phase, although still slightly lower than the 1.5 m NaCl solution. The Crevice Simulation 1-High pH solution has a much higher conductivity than Crevice Simulation 1-Low pH and 1.5 m NaCl at corresponding temperatures. The peak in the Crevice Simulation 1-High pH conductivity curve occurs approximately 25°C lower than that in the sodium sulfate conductivity-temperature curve. The Magnetite buffer solution has a discontinuous increase in conductivity between 200°C and 225°C during the heat up. This is not present in the conductivity-temperature curves of either of the two Crevice Simulation 1 solutions although magnetite is a component of these solutions. The low conductivity at the lower temperatures suggests that equilibrium conditions had not been established within the autoclave. The data during the cooldown did not show the discontinuity and was higher at the lower temperatures which support this conclusion.

Figure 3-3 shows the conductivity-temperature curves for the three pH conditions of the Crevice Simulation 2 solution along with the curves of 1.5 m calcium chloride and sodium sulfate. These are components of the Crevice Simulation 2 solutions but are factors of ten less in concentrations. As in the case of the Crevice Simulation 1 solutions, the high pH condition of the Crevice Simulation 2 solution had the much higher conductivities at corresponding temperatures.

Result and Discussion

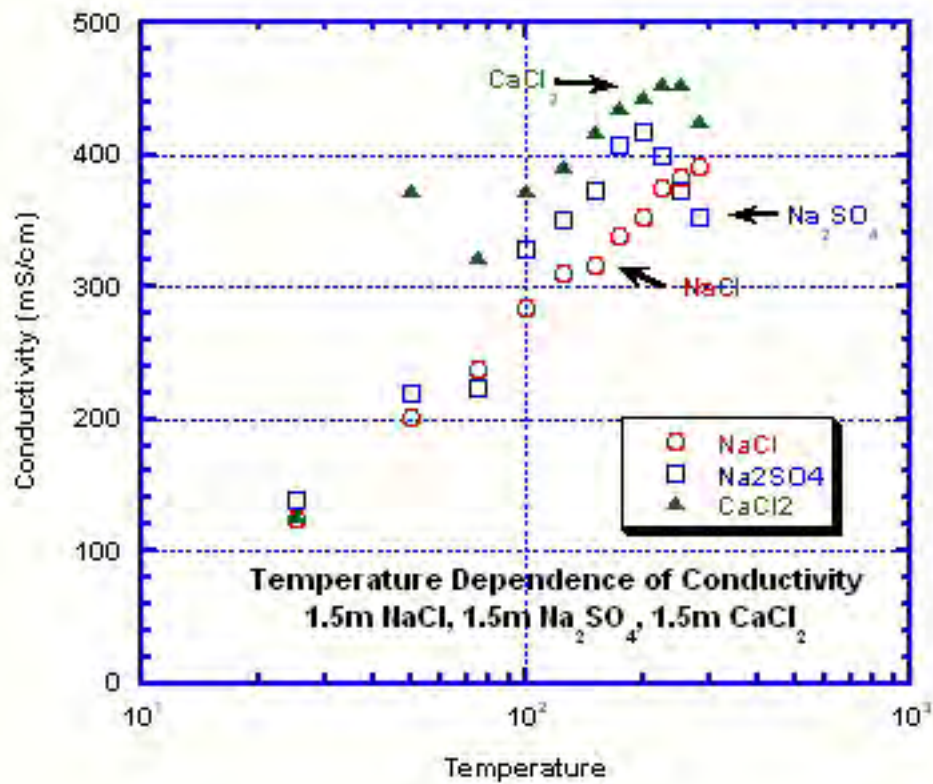


Figure 3-1
Conductivities during Heat-up for 1.5 m Na₂SO₄, 1.5 m CaCl₂, and 1.5 m NaCl Solutions

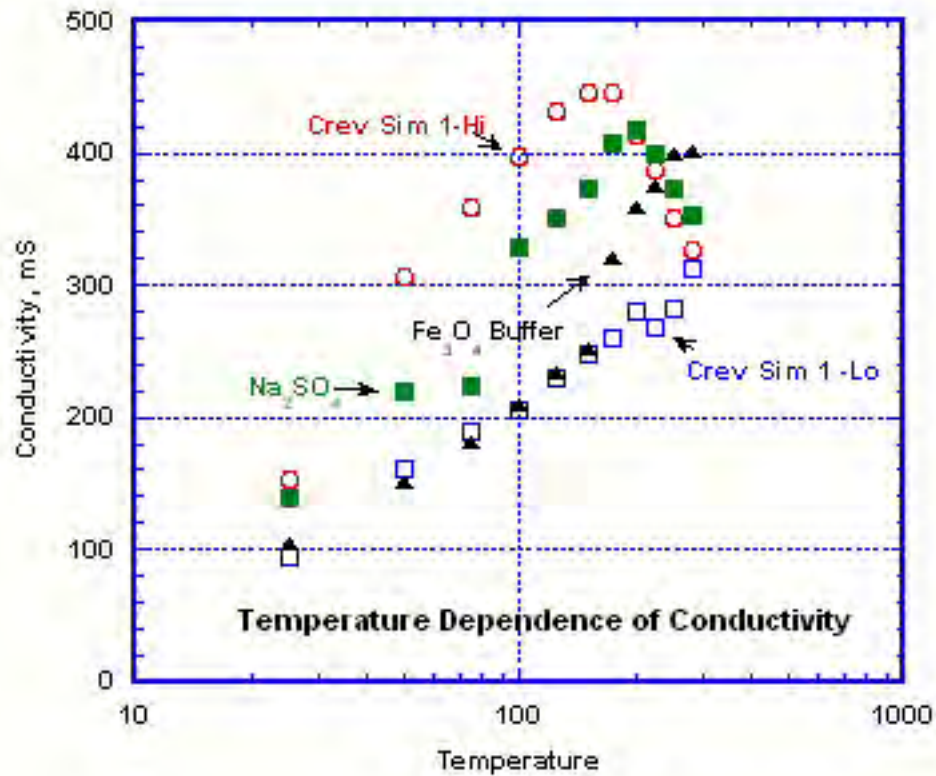


Figure 3-2
Conductivities during Heat-up for Low and High pH Crevice Simulation 1 Solutions,
Magnetite Buffering Solution, and Sodium Sulfate Solution

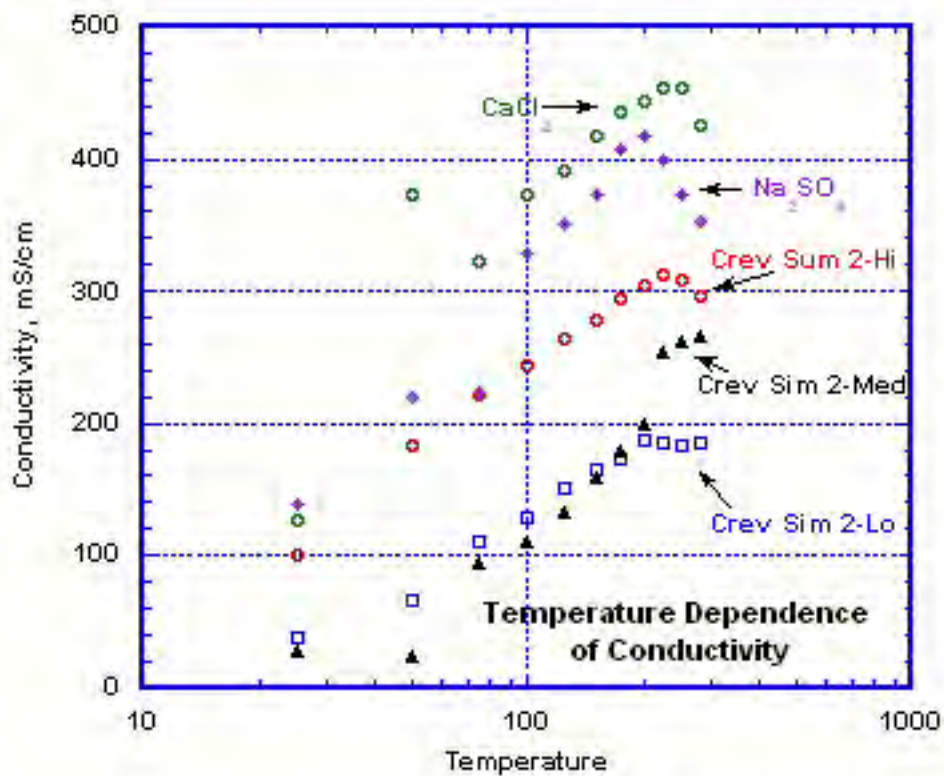


Figure 3-3
Conductivities during Heat-up for the Crevice Simulation 2 Solutions, Calcium Chloride Solution, and Sodium Sulfate Solution

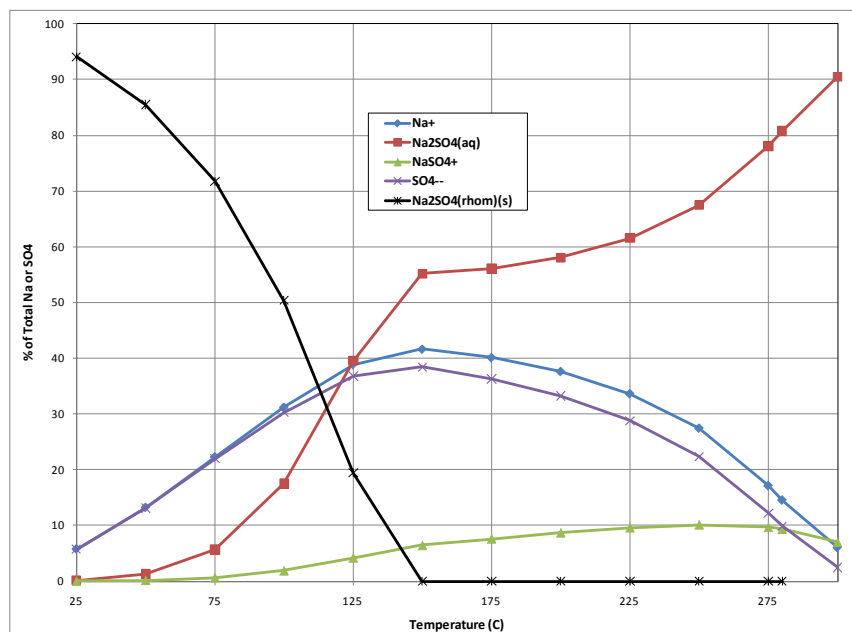


Figure 3-4
MULTEQ Predicted Speciation of 1.5 m Na_2SO_4 Solution

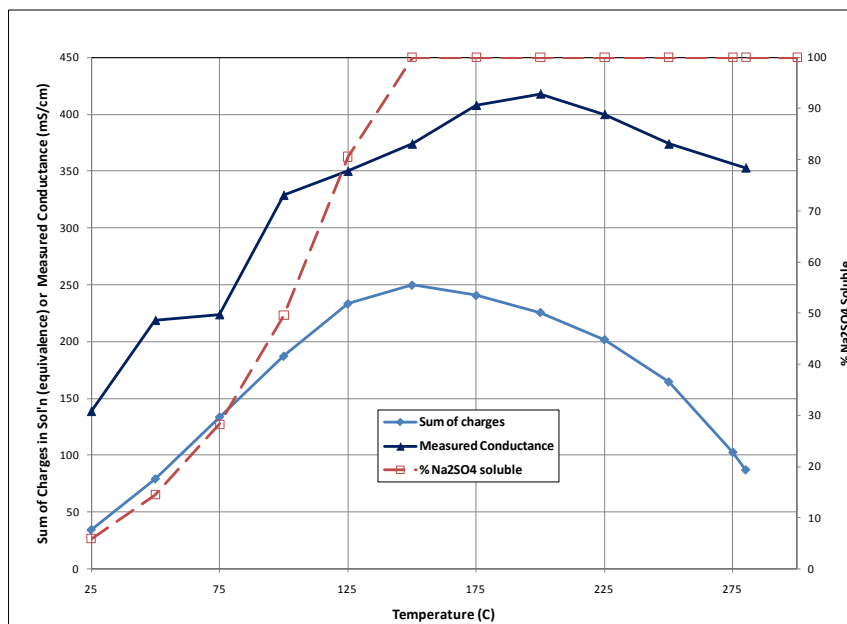


Figure 3-5
Comparison of MULTEQ Predicted Total Ions in Solution with Measured Conductivity

Result and Discussion

The behavior of the temperature dependences of the conductivities for all the solutions during the heat-up and cool-down cycles is shown in Figure 3-6 and can be placed into four groups of increasing complexity. In the first group, the conductivities at corresponding temperatures during heat-up and cool-down of the test solutions are about the same (approximately 5% differences or less at corresponding temperatures). These are the 1.5 m Na₂SO₄, 1.5 m NaCl, Crevice Simulation 2-Low pH, and Crevice Simulation 2-High pH solutions.

The behavior of the conductivity with temperature of the Crevice Simulation 1-Low pH is in a group to itself. Like the 1.5 m NaCl solution, the conductivity increased monotonically with higher temperatures over the entire temperature range investigated. These were the only test solutions in which the conductivity did not reach a peak. However, unlike the NaCl solution, the conductivities of the Crevice Simulation 1-Low pH during cool-down were consistently higher than those during heat-up. This suggests that equilibrium conditions within the autoclave had not been reached during the heat-up.

The third group includes CaCl₂, Crevice Simulation 2-Medium pH (it may be relevant that Crevice Simulation 2 solution contains CaCl₂), and the Magnetite buffering solution. In this group the behavior of the conductivities during heat-up and cool-down at corresponding temperatures were similar but the values of the conductivities at corresponding temperatures differed more than 5%. For example, there was little change in the conductivity of CaCl₂ at the heat-up and cool-down temperatures from 200°C to 280°C, but conductivity at the cool-down temperatures was lower than the corresponding heat-up temperatures. Between room temperature and 200°C the conductivity increased monotonically as the value of the temperature increased, but the cool-down conductivities were slightly higher than the corresponding conductivities during heat-up. Similar behavior is observed for the Crevice Simulation 2-Medium pH and the Magnetite buffering solutions. However, in the latter two solutions the conductivities during cool-down are consistently higher than the corresponding temperatures during heat-up. Discontinuities observed during heat-up were not observed during cool-down. Again, this suggests that equilibrium conditions were not always achieved during the heat-up phase.

The temperature dependence of the conductivity during heat-up and cool-down differed greatest for the Crevice Simulation 1-High pH solution. The conductivity of this solution increased monotonically as the temperature increased until the temperature reached 175°C. During further increase in temperature, the conductivity decreased. During cool-down the conductivity monotonically decreased with temperature and was always much lower than that at the corresponding conductivities during heat-up. All the Crevice Simulation 1 chemistries require dissolution of added solids and precipitation of complex mixtures of aluminum silicates. Kinetics for some of these dissolutions may be slow, and aluminum silicates frequently initially precipitate as amorphous forms which slowly convert to the lower soluble crystalline forms in the MULTEQ database. In addition, there are many possible aluminum silicates. The MULTEQ database contains the aluminum silicates considered most likely to form in steam generators, but others are certainly possible and precipitation of non-stoichiometric products is also possible.

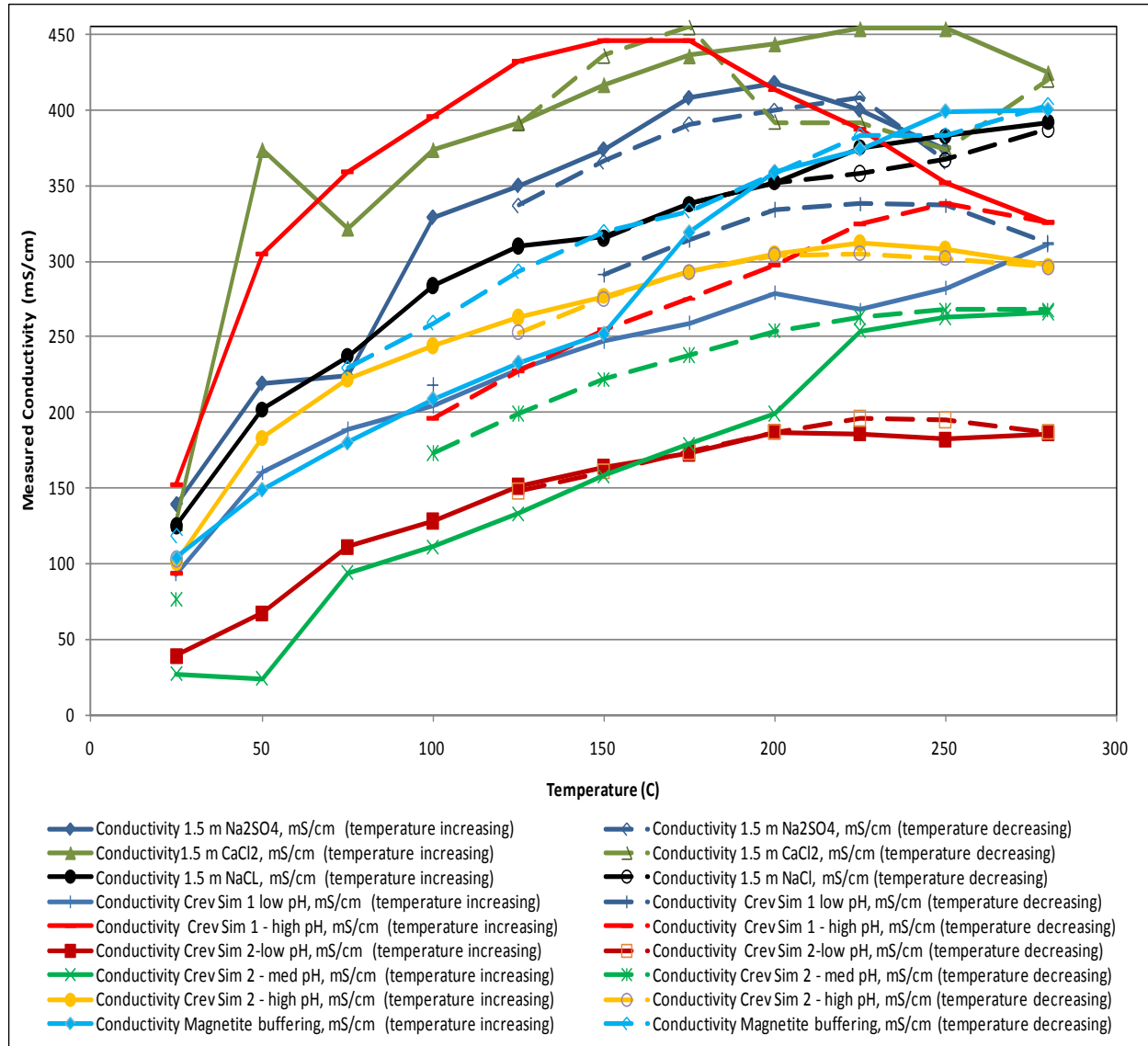


Figure 3-6
Comparison of Measured Conductivities during Heat-up and Cool-down

Result and Discussion

All pH results are given for heat-up conditions. Typically during cool-down the Ag/AgCl reference electrode became unstable, likely due to the formation of bubbles in the reference column. Table 3-11 provides the results for the pH measurements and compares the measured values with the pH calculated using MULTEQ, where the difference between the measured value and the MULTEQ value is indicated as Δ . First noting the extremes, over the entire temperature range the agreement with MULTEQ values is best for sodium sulfate and worst for the Crevice Simulation 1-Low pH. The agreement between MULTEQ values is better at higher pHs than lower pHs. There was a general trend in the temperature dependence that as the temperature decreased the difference between the measured and MULTEQ pH values increased. For example, at 280°C this difference was less than 0.3 pH units for all of the solutions except the two low pH crevice simulations while the differences for these same solutions was 2.5-3.5 pH units at 175°C.

A previous EPRI program compared MULTEQ and measured pH values for borate buffer solutions containing Pb at 280°C [19]. The pH measurements were either the same to the nearest 0.1 pH unit or differed no more than 0.2 pH units from the MULTEQ values, where the 280°C pHs of the test solutions ranged from 6.1 to 9.9. In a later program, solutions that were not buffered were used, having 280°C MULTEQ pH values ranging from 4.0 to 9.0. The results from this second program at 280°C were similar to those in Table 3-11 in that the agreement was best for solutions that were primarily one component and for multi-component in highly alkaline solutions. The worst agreement was for the most acidic, crevice-like solutions having alumina and silica. The concentrations of alumina and silica were similar to those in Crevice Simulation 1 solutions in the present investigation, and several contributors to the disagreement were proposed as follows [18]:

- For the highly acidic solutions, there may have been some corrosion of system materials during heat-up. Generation of soluble metal ions in solution will increase the pH of the low pH solutions.
- For the NaCl solutions with silica, a recently added MULTEQ database entry for lead metasilicate (PbSiO_3) indicates precipitation of this product under the test conditions. Formation of this precipitate would increase the pH slightly.
- The MULTEQ code contains the thermodynamically stable form of the various precipitates. For silica this is the crystalline form of SiO_2 . However, over the short time frame of the test, silica may precipitate as an amorphous product which is more soluble than the crystalline product. This would increase the pH of the low pH solutions and decrease the pH of the near neutral solutions.
- The MULTEQ predictions indicated that almost all the aluminum was precipitated as albite in the complex solutions. Again, the MULTEQ code includes the solubility of the crystalline forms of the various aluminum silicates. Aluminum oxides and silicates are known to frequently supersaturate and precipitate as more soluble amorphous products and then slowly convert to the crystalline forms. Having more aluminum in solution would significantly increase the pH of the low pH solutions. Disabling the albite specie in MULTEQ and allowing the next least soluble aluminum silicates (muscovite, paragonite, nepheline) to define the aluminum concentration in solution results in the predicted pH_{280°C} increasing from 4.0 to approximately 6.5.

It is not totally clear why there was less agreement between measured and MULTEQ values of pH at lower temperatures in this program. Since the operation of the pH electrode depends upon oxygen ion transport to the Cu/Cu₂O couple, it is possible that oxygen ion transport was not efficient at lower temperatures in the zirconia tube used. Communications with the supplier of the pH electrode (Corr Instruments) speculate that the issue is related to non-Nerstian behavior of the Cu/Cu₂O couple. They report a lot of experience with zirconia electrodes giving accurate values of pH down to 90°C. However, those experiences were based upon the internal electrode of the Ag/Ag₂O couple and pH values were determined, not by thermodynamic calculation, but after calibration of the probe using standard solutions.

Figure 3-7 shows a comparison of the measured and predicted pH_T for the 1.5 m NaCl solution. The values are reasonably close at 250°C and 280°C but then diverge at lower temperatures. This simple solution is quite well defined, and the MULTEQ predictions are considered to be accurate. The measured values at the lower temperatures strongly indicate that there is an issue with the measurements at the lower temperatures. If it is assumed that the problem is a calibration issue with the electrode and that the MULTEQ values are accurate, then the measured values can be adjusted to compensate for the measurement error. Specifically, the 1.5 m NaCl solution can be used to calibrate the probe at each temperature. Table 3-12 provides the results of adjusting the measured values using the NaCl solution as a probe calibration solution. The overall agreement over the entire temperature range is much closer than the measured raw values. The low pH crevice simulations still show the greatest disagreement but the difference between adjusted measurements and MULTEQ is much less at the lower temperatures. Crevice Simulation 1-Low pH shows the greatest difference, but the conductivity data indicated that this solution also had the greatest difference in conductivity between heat-up and cool-down so was likely not at chemical equilibrium when the pH measurements were made.

The MULTEQ calculated pH_T is the negative logarithm of the hydrogen ion concentration. The pH electrode response is based on the hydrogen ion activity rather than concentration; i.e., the thermodynamic pH_T. In concentrated solutions at high temperature the difference can be significant. Using the 1.5 m NaCl solution as a calibration solution likely accounted for some of this difference. However, the activity coefficient varies with total solution ionic strength and the test solutions varied somewhat in total ionic strength which would still lead to some differences which not accounted for in Table 3-12. The MULTEQ Database Committee is presently evaluating the issue of thermodynamic pH for inclusion in the code.

Table 3-11
Comparison of Measured pH Values and MULTEQ Values

SOLUTION	pH _{280C}			pH _{250C}			pH _{225C}			pH _{200C}			pH _{175C}		
	Meas'd	MUL'Q	Δ	Meas'd	MUL'Q	Δ	Meas'd	MUL'Q	Δ	Meas'd	MUL'Q	Δ	Meas'd	MUL'Q	Δ
1.5m NaCl	5.31	5.08	0.23	5.4	5.13	0.27	6.66	5.2	1.46	7.67	5.29	2.38	8.9	5.38	3.52
1.5m Na ₂ SO ₄	7.03	7.28	-0.25	7.28	7.01	0.27	7.59	6.93	0.66	7.29	6.91	0.38		6.92	
1.5m CaCl ₂	4.45	4.39	0.06	5.17	4.52	0.65	6.17	4.64	1.53	6.89	4.78	2.11	7.38	4.89	2.49
Crevice Sim 1 - Low pH	8.13	4.08	4.05	7.39	4.01	3.38	9.95	4.3	5.65	10.52	4.61	5.91	11.12	4.91	6.21
Crevice Sim 1 - High pH	9.85	9.53	0.32	9.22	9.67	-0.45	8.88	9.83	-0.95	9.29	10.02	-0.73	13.17	10.27	2.9
Crevice Sim 2 - High pH	9.07	9.27	-0.2	9.29	9.35	-0.06	10.7	9.46	1.24	11.59	9.62	1.97	12.72	9.79	2.93
Crevice Sim 2 - Medium pH	6.09	5.68	0.41	6.12	5.7	0.42	7.09	5.74	1.35	8.21	5.8	2.41	9.29	5.85	3.44
Crevice Sim 2 - Low pH	4.09	2.59	1.5	4.27	2.53	1.74	5.09	2.47	2.62	5.79	2.4	3.39	6.72	2.34	4.38
Magnetite Buffering	3.88	4.14	-0.26	4.17	4.04	0.13	5.08	3.99	1.09	6.03	3.99	2.04	7.15	4.04	3.11

Table 3-12
Comparison of Adjusted Measured pH Values and MULTEQ Values

SOLUTION	pH _{280C}			pH _{250C}			pH _{225C}			pH _{200C}			pH _{175C}		
	Adjusted Meas'd	MUL'Q	Δ	Adjusted Meas'd	MUL'Q	Δ	Adjusted Meas'd	MUL'Q	Δ	Adjusted Meas'd	MUL'Q	Δ	Adjusted Meas'd	MUL'Q	Δ
1.5m NaCl	5.08	5.08	0	5.13	5.13	0	5.2	5.2	0	5.29	5.29	0	5.38	5.38	0
1.5m Na ₂ SO ₄	6.8	7.28	-0.48	7.01	7.01	0	6.13	6.93	-0.8	4.91	6.91	-2.00		6.92	
1.5m CaCl ₂	4.22	4.39	-0.17	4.9	4.52	0.38	4.71	4.64	0.07	4.51	4.78	-0.27	3.86	4.89	-1.03
Crevice Sim 1 - low pH	7.9	4.08	3.82	7.12	4.01	3.11	8.49	4.3	4.19	8.14	4.61	3.53	7.6	4.91	2.69
Crevice Sim 1 - high pH	9.62	9.53	0.09	8.95	9.67	-0.72	7.42	9.83	-2.41	6.91	10.02	-3.11	9.65	10.27	-0.62
Crevice Sim 2 - High pH	8.84	9.27	-0.43	9.02	9.35	-0.33	9.24	9.46	-0.22	9.21	9.62	-0.41	9.2	9.79	-0.59
Crevice Sim 2 - Medium pH	5.86	5.68	0.18	5.85	5.7	0.15	5.63	5.74	-0.11	5.83	5.8	0.03	5.77	5.85	-0.08
Crevice Sim 2 - Low pH	3.86	2.59	1.27	4	2.53	1.47	3.63	2.47	1.16	3.41	2.4	1.01	3.2	2.34	0.86
Magnetite Buffering	3.65	4.14	-0.49	3.9	4.04	-0.14	3.62	3.99	-0.37	3.65	3.99	-0.34	3.63	4.04	-0.41

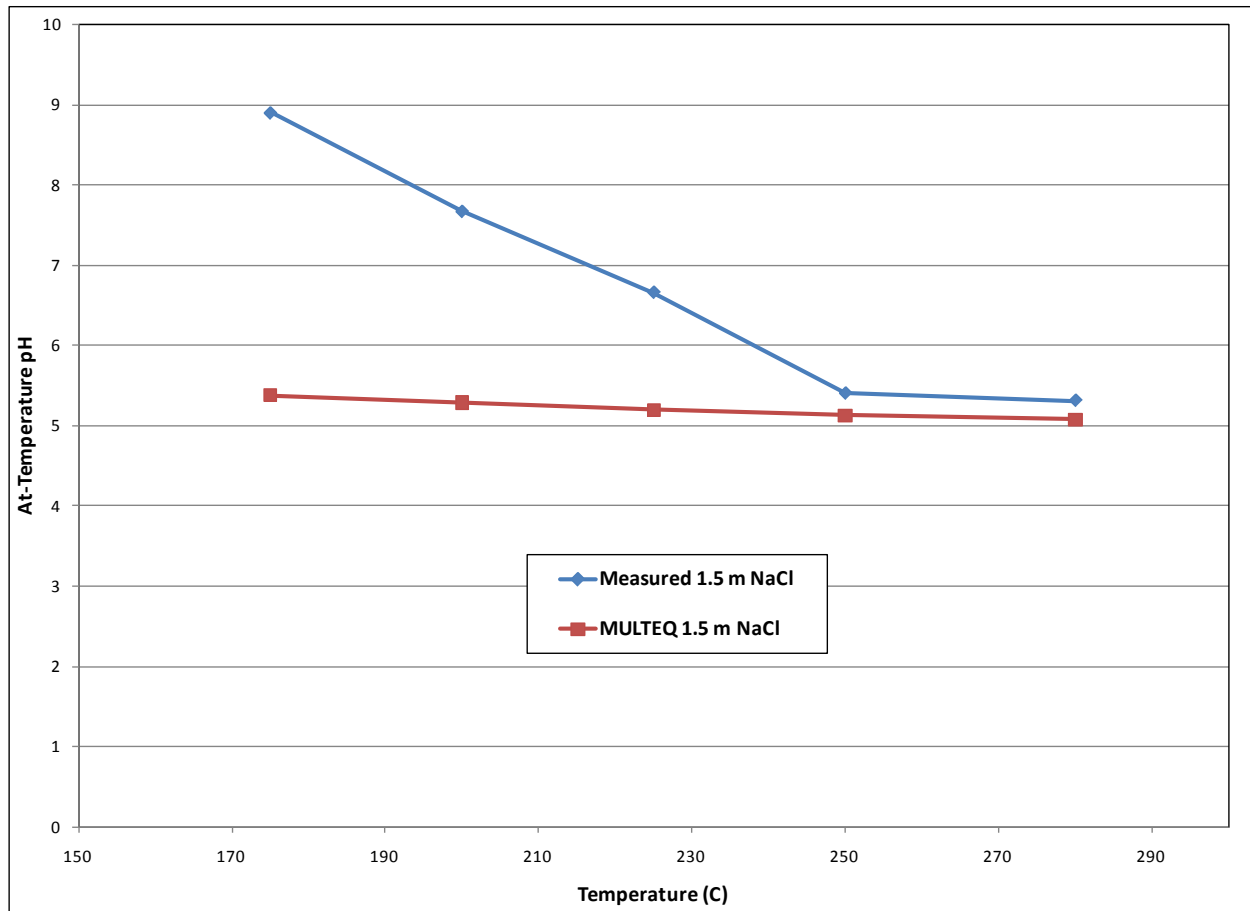


Figure 3-7
Comparison of Measured and MULTEQ Predicted pH Values for 1.5 m NaCl Solution

4

CONCLUSION

- Laboratory investigations were performed to determine the pH and conductivity of test solutions developed by MULTEQ calculations. The conductivity of the test solutions were measured every 25°C between room temperature and 280°C. The at-temperature pH was measured every 25°C from 175°C to 280°C. Based on the results of the laboratory investigations in this study, the following conclusions were made:
- In general, the pH_T agreement between the higher temperature measured values and the MULTEQ calculated values were not large. The agreement was better for the simple solutions than for the more complex solutions. It is likely that some of the more complex solutions were not at chemical equilibrium when the pH measurements were made.
- The measured values at the lower temperatures were clearly not accurate. Using the 1.5 m NaCl solution as a calibration solution resulted in much more reasonable values and better agreement between measured and calculated values at the lower temperatures.
- The conductivity measurements during heat-up and cool-down indicated that chemical equilibrium had not been established for some of the complex solutions. This was especially true for the more complex crevice simulations.
- The predicted $\text{pH}_{280\text{C}}/\text{pH}_{250\text{C}}$ for the magnetite buffer solution without any of the magnetite dissolving is approximately 1.7. The measured values were 3.88/4.17 (raw) and 3.65/3.90 (adjusted) compared to the MULTEQ predicted 4.14/4.04 values. This data supports the hypothesis that extremely low pH will not likely to occur in operating steam generator crevices due to magnetite dissolution.
- The conductivity data for the CaCl_2 solution suggest that a combination specie such as CaCl^+ may form at high temperature in solutions with high calcium and chloride concentrations.
- For the highly acidic solutions, there may have been some corrosion of system materials during heat-up. Generation of soluble metal ions in solution will increase the pH of the low pH solutions.
- The MULTEQ code contains the thermodynamically stable form of the various precipitates. For silica this is the crystalline form of SiO_2 . However, over the short time frame of the test, silica may precipitate as an amorphous product which is more soluble than the crystalline product. This would increase the pH of the low pH solutions and decrease the pH of the near neutral solutions.
- The MULTEQ predictions indicated that almost all the aluminum was precipitated in the complex solutions. Again, the MULTEQ code includes the solubility of the crystalline forms of the various aluminum silicates. Aluminum oxides and silicates are known to frequently supersaturate and precipitate as more soluble amorphous products and then slowly convert to

Conclusion

the crystalline forms. Having more aluminum in solution would significantly increase the pH of the low pH solutions.

- Installation of a stirrer into the autoclave system would provide more reliable mixing and could also lead to faster kinetics with respect to achieving equilibrium conditions.
- The data from this study should be re-evaluated with respect to the thermodynamic pH_T after the MULTEQ Database Committee defines the most appropriate calculation of this parameter.
- It is recommended that the MULTEQ Database Committee review the results of this project and evaluate if any modifications to the database are warranted.

5

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APPENDIX—(PREPARED BY R. EAKER)

Summary of Test Solution Compositions

Recommendations for the ten solutions to be tested are based on evaluating MULTEQ activity coefficient assumptions, previous corrosion tests, solutions being evaluated in EPRI Project 1.4.28, and simulated possible complex crevice environments. The solutions cover a broad range of pH_T values and solution compositions. The recommended solution compositions are:

1. 1.5 m NaCl
2. 1.5 m CaCl_2
3. 1.5 m Na_2SO_4
4. Crevice Simulation 1-low pH: 1.5 m NaCl + 0.25 m Na_2SO_4 + 0.3 m SiO_2 + 0.075 m Al_2O_3 + 0.00333 m Fe_3O_4 + 0.0318 m PbO
5. Crevice Simulation 1-medium pH: This solution is the same composition as item d. above but with the addition of 0.12 m KOH
6. Crevice Simulation 1-high pH: This solution is the same composition as item d. above but with the addition of 0.50 m KOH
7. Crevice Simulation 2-medium pH: 0.3 m NaCl + 0.15 m Na_2SO_4 + 0.15 m CaCl_2 + 0.05 m KCl
8. Crevice Simulation 2-high pH: This solution composition is the same as item g. above but with the addition of 0.40 m NaOH
9. Crevice Simulation 2-low pH: This solution composition is the same as item g. above but with the addition of 0.05 m NaHSO_4
10. Magnetite buffering solution: 1.5 m NaCl + 0.02 m HCl + 0.03333 m Fe_3O_4 .

A summary of the MULTEQ predicted pH_T values for 175°C - 280°C are provided in Table A-1. Additional details and discussion of the basis for the recommendations and the predicted species distributions for each solution are provided in Section 3 of this report.

Table A-1
Summary of MULTEQ pH_T Predictions for Ten Recommended Solutions

Solution	Temperature, °C				
	175	200	225	250	280
1.5 m NaCl	5.40	5.29	5.20	5.13	5.08
1.5 m CaCl ₂	4.89	4.78	4.64	4.52	4.39
1.5 m Na ₂ SO ₄	6.91	6.90	6.92	6.99	7.27
Crevice simulation 1 - low pH	4.91	4.61	4.30	4.01	4.08
Crevice simulation 1 - med pH	8.49	8.04	7.64	7.28	6.90
Crevice simulation 1 - high pH	10.26	10.02	9.82	9.67	9.52
Crevice simulation 2 - low pH	2.07	2.40	2.47	2.53	2.59
Crevice simulation 2 - med pH	5.86	5.80	5.74	5.70	5.68
Crevice simulation 2 - high pH	10.42	9.62	9.46	9.35	9.27
1.5 m NaCl + 0.02 m HCl + 0.01 m Fe added as Fe ₃ O ₄	4.05	3.99	3.99	4.04	4.14

Calculations and Recommendations

Chemistry compositions and pHs were calculated using EPRI ChemWorks MULTEQ using Version 5.0 of the database. All the pH values in this report are calculated values and are shown to two decimal points. The calculations are likely not that accurate with respect to actual pH values but the two decimal points are shown to better understand the trends. The autoclave will be started up with a 5% H₂ gas phase. Therefore, 6 ppm H₂ (0.003 m H₂) was added to each MULTEQ run to simulate the estimated hydrogen concentration in the liquid phase. The primary purpose of the project is to generate data to verify that the MULTEQ calculations are reasonable. MULTEQ is used in various applications from simple solutions for laboratory testing to complex solutions based on operating steam generator hideout return.

- Several issues were investigated in evaluation of solutions to be recommended. MULTEQ uses an activity coefficient model based on NaCl. This should result in the MULTEQ outputs being most accurate for NaCl solutions and other similar 1:1 electrolytes. Therefore, the first recommended solution is a simple solution as a baseline to compare to more complex solutions. A solution 1.5 m Na⁺ and 1.5 m Cl⁻ can be made up by adding 1.5 m NaCl to the solution. MULTEQ calculated pH_Ts for this solution are shown in Table A-1 and Figure A-1. This solution should be completely soluble at all temperatures and dimer formation is predicted to be insignificant.
- Activity coefficients for divalent species may be somewhat less accurate. The next two solutions are recommended as a test to validate the MULTEQ calculations for 2:1 electrolytes. A simple 1.5 m CaCl₂ solution is recommended as a test for a divalent cation species. This solution will be 1.5 m Ca⁺ and 3 m Cl⁻. It should be completely soluble at all temperatures with insignificant dimer formation. MULTEQ calculated pH_Ts for this solution are shown in Table A-1 and Figure A-1.

- A simple 1.5 m Na₂SO₄ solution is recommended as a test for a divalent anion species and as a test of the sulfate model. Sulfate is a commonly seen species in hideout return, and the sulfate model in MULTEQ is important in pH predictions involving sulfate species. The sulfate model has been revised several times as MULTEQ has been updated. This solution will be 3 m Na⁺ and 1.5 m SO₄⁻. It should be completely soluble at all temperatures. MULTEQ predicted pH_T values are shown in Table A-1 and Figure A-1. This solution is predicted to have significant dimer and trimer formation at 180°C - 300°C. At 300°C the sodium species in solution are predicted to be approximately 90% Na₂SO₄(aq), 6% Na⁺, and 3.5% NaSO₄⁻. At 150°C the sodium species in solution are predicted to be approximately 55% Na₂SO₄(aq), 41% Na⁺, and 3.5% NaSO₄⁻.
- It is recommended that some of the solutions to be tested be similar to the compositions of the solutions used in corrosion tests shown in EPRI 1009532 and 1013640. The results of these tests are frequently used for PbSCC evaluations and Alloy 690TT/600MA factor of improvement estimates. The simple NaCl solutions used in these tests are reasonably represented in ECP testing planned in EPRI project 1.4.32. Since at-temperature pH will also be measured during the ECP tests, it recommended these solutions not be duplicated in this project. It was originally intended to test the older very complex crevice simulation used in the corrosion tests as part of this project. This solution was 1.5 m Na₂SO₄ + 0.01 m Fe₃O₄ + 0.05 m Al₂O₃ + 0.3 m SiO₂ + 0.15 m KOH + 0.04 m HCl with an indicated MULTEQ calculated pH_{330C} of 9. However, attempts to define pH_T and species distributions for this solution with the ChemWorks MULTEQ Version 5 resulted in code convergence not being achieved. Therefore, the estimated pH_T was not trustworthy and no species distribution was defined in the code output. The older DOS version of MULTEQ did frequently achieve convergence with results similar to that indicated in the corrosion reports. However, the results/convergence were found somewhat variable with minor changes in the inputs and were not considered highly reliable. Therefore, somewhat diluted solutions of similar composition are recommended for this test program. Three solutions of similar composition but adjusted to different pH_T values are recommended to represent possible crevice solutions. These solutions will be referred to Crevice Simulations 1 in this report.

Crevice Simulation 1-Low pH: This solution is 2.0 m Na, 1.5 m Cl, 0.25 m SO₄, 0.3 m Si, 0.15 m Al, 0.01 m Fe, and 0.0318 m Pb (6595 ppm Pb). It can be made up by adding 1.5 m NaCl, 0.25 m Na₂SO₄, 0.3 m SiO₂, 0.075 m Al₂O₃, 0.00333 m Fe₃O₄ and 0.0318 m PbO to the autoclave solution. (Note that the intended Pb concentration was originally 500 ppm Pb, but the actual concentration used was higher due to an error in the original conversion from ppm to molal when performing these calculations and transmitting the values to Teledyne. The speciation estimates in this section have been revised from the original estimates to the actual concentration used.) The predicted species distributions at 280°C are:

1. Na: 78.2% Na⁺, 15.2% Na₂SO₄(aq), 3.6% Albite(s), 0.8% NaHSO₄(aq), 0.8% NaSO₄, 1.3% Paragonite(s)
2. SO₄: 60.6% Na₂SO₄(aq), 6.7% NaHSO₄(aq), 12.5% SO₄²⁻, 4.5% HSO₄⁻, 6.8% NaSO₄⁻, 8.9% PbSO₄(s)
3. Si: 72.6% Albite(s), 25.8% Paragonite(s)
4. Al: 51.6% Paragonite(s), 48.4% Albite(s)

5. Pb: 69.7% $\text{PbSO}_4(\text{s})$, 24.8% PbCl_3^- , 4.9% $\text{PbCl}_2(\text{aq})$, 0.6% PbCl^+

Crevice Simulation 1-Medium pH: This solution is the same as the Low pH Crevice Simulation 1 but with the addition of 0.12 m KOH to raise the pH. It can be made up by adding 1.5 m NaCl, 0.25 m Na_2SO_4 , 0.3 m SiO_2 , 0.12 m KOH, 0.075 m Al_2O_3 , 0.00333 m Fe_3O_4 and 0.0318 m PbO to the autoclave solution. The predicted species distributions at 280°C are:

1. Na: 75.3% Na^+ , 18.4% $\text{Na}_2\text{SO}_4(\text{aq})$, 3.1% Albite(s), 1.2% NaSO_4^- , 2% Nepheline(s)
2. SO_4 : 73.8% $\text{Na}_2\text{SO}_4(\text{aq})$, 8.8% NaSO_4^- , 17.4% SO_4^{2-}
3. Si: 62.3% Albite(s), 11.3% Nepheline(s), 15.8% Muscovite(s)
4. Al: 31.6% Muscovite(s), 41.6% Albite(s), 26.6% Nepheline(s)
5. Pb: 12.9% Pb(m), 78.0% $\text{PbSO}_4(\text{s})$, 3.8% PbCl_3^- , 0.7% $\text{PbCl}_2(\text{aq})$, 0.4% $\text{Pb}(\text{OH})_2(\text{aq})$, 4.1% PbOH^+ , 0.1% PbCl^+

Crevice Simulation 1-High pH: This solution is the same as the Low pH Crevice Simulation 1 but with the addition of 0.50 m KOH to raise the pH. It can be made up by adding 1.5 m NaCl, 0.25 m Na_2SO_4 , 0.3 m SiO_2 , 0.50 m KOH, 0.075 m Al_2O_3 , 0.00333 m Fe_3O_4 and 0.0318 m PbO to the autoclave solution. The predicted species distributions at 280°C are:

1. Na: 74.6% Na^+ , 16.3% $\text{Na}_2\text{SO}_4(\text{aq})$, 2% Albite(s), 1.2% NaSO_4^- , 0.5% $\text{NaOH}(\text{aq})$, 5.5% Nepheline(s)
 2. SO_4 : 65.1% $\text{Na}_2\text{SO}_4(\text{aq})$, 9.8% NaSO_4^- , 24.4% SO_4^{2-} , 0.4% KSO_4^-
 3. Si: 40.0% Albite(s), 36.6% Nepheline(s), 3% $\text{H}_2\text{SiO}_4^{2-}$, 13.1% H_3SiO_4^- , 0.2% $\text{H}_4\text{SiO}_4(\text{aq})$, 7.1% $\text{PbSO}_4(\text{s})$
 4. Al: 26.7% Albite(s), 73.1% Nepheline(s), 0.2% $\text{Al}(\text{OH})_4^-$
 5. Pb: 67.2% $\text{PbSiO}_3(\text{s})$, 12.7% Pb(m), 19.5% $\text{Pb}(\text{OH})_3^-$, 0.4% $\text{Pb}(\text{OH})_2(\text{aq})$
- In addition to the crevice simulations above, three additional crevice simulations are recommended for this test program. These simulations are similar to solutions used by AECL as representative of possible crevice solutions. They are more dilute than the Crevice Simulation 1 solutions, less complex, and contain relatively higher sulfate and some calcium. They may be representative of regions in the operating steam generators where concentration factors are lower than deep crevice situations. Again, three solutions of similar composition but adjusted to low, medium, and high pH values are recommended. They will be referred to as Crevice Simulation 2:

Crevice Simulation 2-Medium pH: This solution is 0.60 m Na, 0.65 m Cl, 0.15 m SO_4 , 0.05 m K, and 0.15 m Ca. It can be made up by adding 0.3 m NaCl, 0.15 m Na_2SO_4 , 0.15 m CaCl_2 , and 0.05 m KCl to the autoclave solution. The predicted species distributions at 280°C are:

1. Na: 99% Na^+
2. SO_4 : 98% $\text{CaSO}_4(\text{s})$, 1% $\text{Na}_2\text{SO}_4(\text{aq})$
3. Ca: 98% $\text{CaSO}_4(\text{s})$, 2% Ca^{2+}

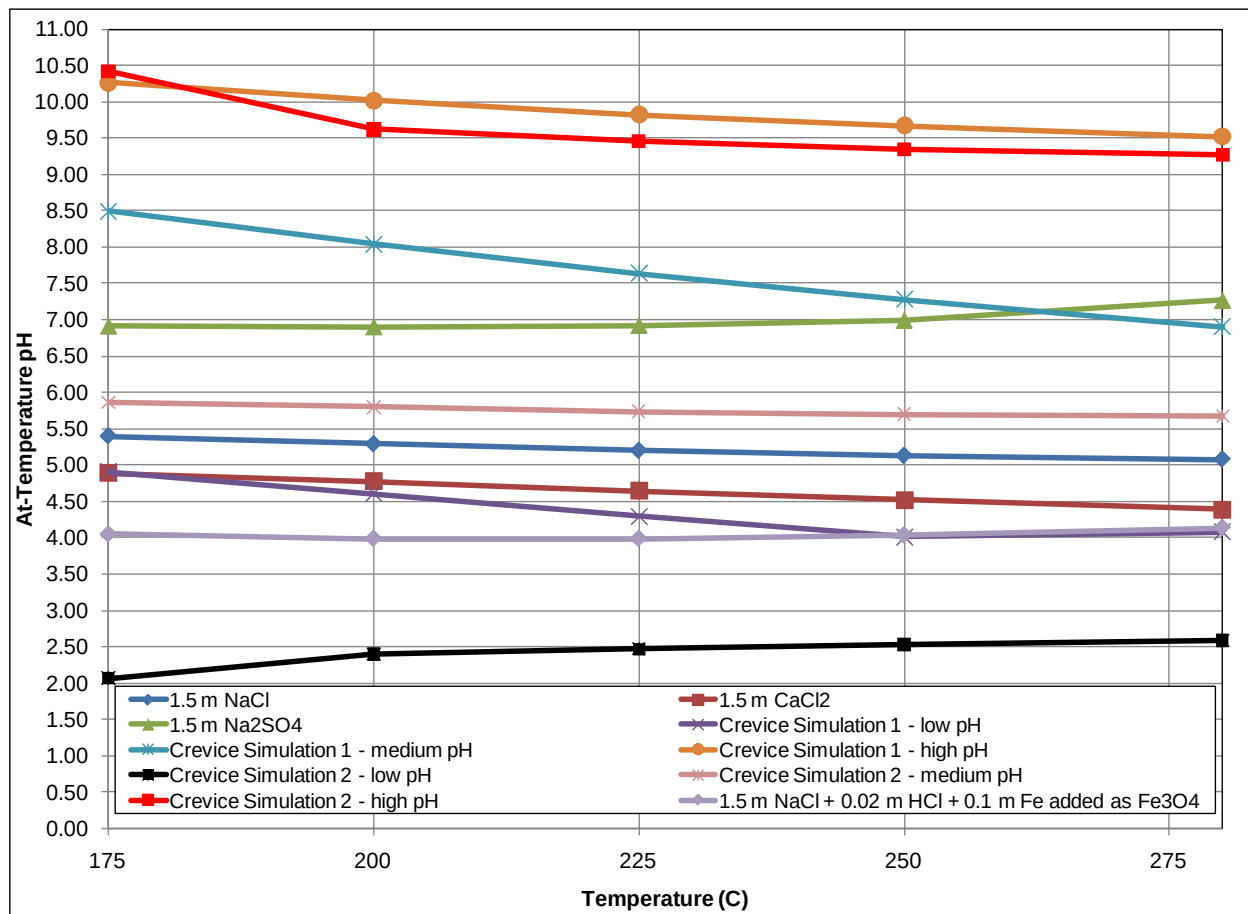
Crevice Simulation 2-High pH: This solution is the same as the above Crevice Solution 2-Medium pH but with the addition of 0.04 m NaOH. The predicted species distributions at 280°C are:

1. Na: 71% Na^+ , 21% $\text{Na}_2\text{SO}_4(\text{aq})$
2. SO_4 : 71% $\text{Na}_2\text{SO}_4(\text{aq})$, 19% SO_4^{2-} , 9% NaSO_4^-
3. Ca: 100% $\text{Ca}(\text{OH})_2(\text{s})$

Crevice Simulation 2-Low pH: This solution is the same as the above Crevice Solution 2-Medium pH but with the addition of 0.05 m NaHSO_4 . The predicted species distributions at 280°C are:

1. Na: 95% Na^+ , 4% $\text{NaHSO}_4(\text{aq})$, 1% $\text{Na}_2\text{SO}_4(\text{aq})$
 2. SO_4 : 74% $\text{CaSO}_4(\text{s})$, 12% $\text{NaHSO}_4(\text{aq})$, 11% HSO_4^-
 3. Ca: 99% $\text{CaSO}_4(\text{s})$, 1% Ca^{2+}
- The final recommended solution is intended to test the prediction that extremely low pH will not be obtained in a crevice because the dissolution of magnetite will buffer to above approximately pH_T of 3.5 or higher. The recommended solution is 1.5 m NaCl + 0.02 m HCl + 0.03333 m Fe_3O_4 . The predicted pH of this solution without the iron added is 1.70-1.75 between 150°C and 300°C. The predicted pHs with the iron added is slightly above 4. Note that MULTEQ does not allow for adding a solid phase as magnetite. At 280°C, the final solution was predicted to have 10% of the iron in solution and 88% as magnetite and 2% as hematite. If some of the dissolved magnetite ends up in other forms the actual pH may vary from the predicted values.

Appendix—(Prepared by r. Eaker)

**Table A-2****At Temperature pH as a Function of Temperature for Recommended Solutions**

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