Deliquescence of NaCl–NaNO₃, KNO₃–NaNO₃, and NaCl–KNO₃ salt mixtures from 90 to 120 °C

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We conducted reversed deliquescence experiments in saturated NaCl–NaNO₃–H₂O, KNO₃–NaNO₃–H₂O, and NaCl–KNO₃–H₂O systems from 90 to 120 °C as a function of relative humidity and solution composition. NaCl, NaNO₃, and KNO₃ represent members of dust salt assemblages that are likely to deliquesce and form concentrated brines on high-level radioactive waste package surfaces in a repository environment at Yucca Mountain, NV. Discrepancy between model prediction and experiment can be as high as 8% for relative humidity and 50% for dissolved ion concentration. The discrepancy is attributed primarily to the use of 25 °C models for Cl–NO₃ and K–NO₃ ion interactions in the current Yucca Mountain Project high-temperature Pitzer model to describe the nonideal behavior of these highly concentrated solutions. © 2005 American Institute of Physics. [DOI: 10.1063/1.1872292]

I. INTRODUCTION

Yucca Mountain, NV is the designated geologic repository for permanent disposal of high-level nuclear waste. Current waste package design calls for double walled containers with an inner wall of stainless steel and an outer wall of highly corrosion resistant Ni–Cr–Mo alloy, which are protected with Ti shields to prevent rocks and seepage water from contacting the containers. Of concern are the corrosion resistance and long-term integrity of these metal barriers. If the Yucca Mountain site license is approved, the waste packages will be placed in tunnels several hundred meters below the ground surface in partially saturated volcanic tuff, but still well above the groundwater table. A likely source of brines that may potentially corrode metal containers and drip shields are those formed by the absorption of water by hygroscopic salts found in local and regional dust deposited during repository construction and ventilation stages.

Accurate prediction of brine formation is important for the safe disposal of radioactive waste, because brine composition is an indicator of the corrosiveness of the aqueous environment and the relationship between deliquescence relative humidity and temperature is an indicator of "repository dryness." Deliquescence refers to the formation of an aqueous solution by the absorption of water by hygroscopic salt minerals. This process allows brines to form above an aqueous solution by the absorption of water by hygroscopic crystals. For example at 90 °C, MgCl₂ deliquesces at 24% relative humidity. Generally, the deliquescence relative humidity for a salt mixture is lower than the deliquescence relative humidity for its pure salt components. Salt deliquescence data are largely limited to 25 °C for mixed salts but are widely available for single salts at higher temperatures.

The range of brines formed by the deliquescence of hygroscopic salts found in dusts can be calculated from mixtures of the pure phases using equilibrium thermodynamics, because relative humidity is related to the activity of water and solution composition. Wolery and Wang used the EQ3/6 geochemical code and the Yucca Mountain Project high-temperature Pitzer model to predict the deliquescence of salt mixtures found in Yucca Mountain dust samples collected from exploratory tunnels. The modeling results predict that mixtures of NaCl, KNO₃, and/or NaNO₃ are the most prevalent mineral assemblages, and that inclusion of KNO₃ lowers the deliquescence relative humidity from values near 70% at 25 °C to values as low as 20% at 160 °C. This analysis implies that concentrated brines may contact the metal container and drip shield surfaces at low relative humidity and high temperature.

In this paper we compare model predictions and experimental results of relative humidity and solution compositions for saturated NaCl–NaNO₃–H₂O, KNO₃–NaNO₃–H₂O, and NaCl–KNO₃–H₂O systems from 90 to 120 °C. These are benchmark experiments that can be used to assess the validity of the model calculations and Pitzer parameters that account for nonideal ion interactions in these highly concentrated solutions.

II. MODEL CALCULATIONS

Relative humidity is thermodynamically tied to solution composition through the activity of water. For water, its activity, \( a_w \), is the product of its mole fraction, \( x_w \), and its mole fraction activity coefficient, \( \gamma_w \): \( a_w = x_w \gamma_w \). \( \gamma_w \) denotes the activity coefficient of water.

The mole fraction of water is dependent on the solution composition:
The activity of water is commonly expressed in decimal form and RH is commonly expressed as a percentage; thus RH\% = 100 \times a_w.\)

In hydrologically unsaturated environments, the partial pressure of water cannot exceed the total pressure. The partial pressure of water is related to the vapor pressure of pure water and the activity of water by $p_w = p_w^0 a_w$. Both the vapor pressure of pure water and the partial pressure of water over a salt solution increase strongly with temperature above 100 °C. Brines cannot exist at temperatures above the dry-out temperature, where the partial pressure of water equals the total pressure. Above the dry-out temperature only solid salt minerals and water vapor occur. Since this process is reversible, the dry-out temperature is also the deliquescence temperature for the same assemblage of salt minerals (note: at much lower temperature, generally 25 °C or less, dry-out or "efflorescence" is controlled by salt mineral nucleation instead of equilibrium thermodynamics.\(^5\) The deliquescence temperature is also equivalent to the boiling point for the saturated solution.

Brines formed by the absorption of water by deliquescent minerals are thermodynamically equivalent to brines that are saturated with respect to the same deliquescent minerals. Figures 1–5 show the model calculations of relative humidity and solution composition from 90 to 120 °C versus $X_{NO3}$ or $X_{Na}$ for the NaCl–NaNO₃–H₂O, the KNO₃–NaNO₃–H₂O, and the NaCl–KNO₃–H₂O systems. For the NaCl–NaNO₃–H₂O system, this is done by adding soda niter (NaNO₃) to a halite (NaCl) saturated solution until the solution is saturated with both soda niter and halite. This represents the eutonic point for the NaCl–NaNO₃ salt assemblage. The calculation for this assemblage is completed by a complementary run in which halite is added to a soda niter saturated solution until the same eutonic point is
reached. An identical approach is used for the KNO₃-NaNO₃-H₂O and NaCl-KNO₃-H₂O systems. We use the EQ3/6 geochemical code and the Yucca Mountain Project high-temperature Pitzer model. This model is based on the Pitzer equations (cf. Ref. 9) to account for the non-ideal behavior of the brine solutions. Reaction pressure was allowed to vary by means of the 1.013 bar/steam-saturation curve. The Pitzer model is based on the available experimental data and includes binary interactions between two different kinds of ions of opposite charge (cation M and anion X), and also binary (θₓₓ,θₓₓ) interactions between ions of like charge and ternary interactions (ψₓₓ,ₓₓ,ₓₓ) involving three ions in common-cation and common-anion ternary systems. Pitzer parameters relevant to this study are listed in Table I.

III. EXPERIMENTAL METHODS
A. Starting materials
Analytical grade sodium chloride (NaCl, 100.1% pure), sodium nitrate (NaNO₃, 99.7% pure), and potassium nitrate (KNO₃, 99.5% pure) were used to synthesize dissolved and dry salt mixtures. Impurities in NaCl include less than 0.01%
Br; 0.005% K; 0.004% SO$_4$, 0.003% ClO$_4$, NO$_3$, and Ba; 0.002% I and Ca; 0.001% Mg; 5 ppm PO$_4$; 2 ppm heavy metals, and 1 ppm Fe. Impurities in NaNO$_3$ include less than 0.002% K; 0.001% SO$_4$, NO$_2$, Ca, Mg, and R$_2$O$_3$; 0.0005% Cl; 3 ppm PO$_4$ and heavy metals, and 1 ppm Fe and IO$_3$. Impurities in KNO$_3$ include less than 0.004% Na; 0.002% SO$_4$; 0.001% Cl, and NO$_2$, 0.0005% Ca; 0.0002% Mg; 3 ppm heavy metals, 2 ppm PO$_4$ and 1 ppm Fe and IO$_3$. Distilled and de-ionized (18 MΩ) water was used to make all solutions.

**B. Reverse deliquescence experiments**

We measured brine composition at controlled relative humidity for NaCl–NaNO$_3$, KNO$_3$–NaNO$_3$, and NaCl–KNO$_3$ salt mixtures from 90 to 120 °C as a function of X$_{NO3}$ or X$_{Na}$. Our experimental design mimics the model calculations in that one salt in the binary system will completely dissolve and the dissolution of the other will be limited by its solubility. We approached the equilibrium brine composition by placing identical mole fractions of dissolved...
TABLE I. Pitzer interaction parameters used with EQ3/6 to calculate relative humidity and solution composition in saturated brines containing Na, K, Cl, and NO₃. Temperature dependence of each of these ion interaction parameters is derived from Eq. (11): \( \chi(T) = a_1 + a_2/\left(T - T_r\right) + a_3 \ln(T/T_r) + a_4 \).

| Ion interactions | Coefficients | \( a_1 \) | \( a_2 \) | \( a_3 \) | \( a_4 \) | Reference |
|------------------|--------------|----------|----------|----------|----------|-----------|
| K–Cl             | \( \beta_{\text{MX}}^{11} \) | \( 4.78 \times 10^{-02} \) | \( -3.43 \times 10^{-02} \) | \( -1.38 \) | \( 1.34 \times 10^{-03} \) | 10 |
|                  | \( \beta_{\text{MX}}^{10} \) | \( 2.16 \times 10^{-01} \) | \( -5.76 \times 10^{-02} \) | \( -2.88 \) | \( 4.64 \times 10^{-03} \) | 10 |
|                  | \( \beta_{\text{MX}}^{00} \) | 0.00     |          |          |          | 10        |
|                  | \( C_{\text{MX}} \) | \( -7.49 \times 10^{-04} \) | \( 3.65 \times 10^{-01} \) | \( 1.48 \times 10^{-01} \) | \( -1.47 \times 10^{-04} \) | 10 |
| K–NO₃           | \( \beta_{\text{MX}}^{11} \) | \( -8.16 \times 10^{-02} \) |          |          |          | 9         |
|                  | \( \beta_{\text{MX}}^{10} \) | 4.94 \times 10^{-02} |          |          |          | 9         |
|                  | \( \beta_{\text{MX}}^{00} \) | 0.00     |          |          |          | 9         |
|                  | \( C_{\text{MX}} \) | \( 6.60 \times 10^{-03} \) |          |          |          | 9         |
| Na–Cl           | \( \beta_{\text{MX}}^{11} \) | \( 7.46 \times 10^{-02} \) | \( -4.71 \times 10^{-02} \) | \( -1.85 \) | \( 1.66 \times 10^{-03} \) | 10 |
|                  | \( \beta_{\text{MX}}^{10} \) | \( 2.75 \times 10^{-01} \) | \( -5.21 \times 10^{-02} \) | \( -2.88 \) | \( 4.71 \times 10^{-03} \) | 10 |
|                  | \( \beta_{\text{MX}}^{00} \) | 0.00     |          |          |          | 10        |
|                  | \( C_{\text{MX}} \) | \( 1.54 \times 10^{-03} \) | \( 4.81 \times 10^{-01} \) | \( 1.75 \times 10^{-01} \) | \( -1.56 \times 10^{-04} \) | 10 |
| Na–NO₃          | \( \beta_{\text{MX}}^{11} \) | \( 3.57 \times 10^{-03} \) | \( -7.03 \times 10^{-02} \) | \( -3.35 \) | \( 3.98 \times 10^{-03} \) | 11 |
|                  | \( \beta_{\text{MX}}^{10} \) | \( 2.32 \times 10^{-01} \) | \( -2.73 \times 10^{-03} \) | \( -1.30 \times 10^{-01} \) | \( 2.07 \times 10^{-02} \) | 11 |
|                  | \( \beta_{\text{MX}}^{00} \) | 0.00     |          |          |          | 11        |
|                  | \( C_{\text{MX}} \) | \( -4.15 \times 10^{-05} \) | \( 6.48 \times 10^{-01} \) | \( 3.18 \times 10^{-01} \) | \( -3.84 \times 10^{-04} \) | 11 |
| K–Na            | \( s_{\theta_{\text{MM}}} \) | \( -3.20 \times 10^{-03} \) | \( 1.40 \times 10^{-01} \) | \( 9.09 \times 10^{-13} \) | \( -2.66 \times 10^{-15} \) | 10 |
| Cl–NO₃         | \( s_{\theta_{\text{XX}}} \) | \( 1.60 \times 10^{-02} \) |          |          |          | 9         |
| K–Na–Cl        | \( \phi_{\text{MM/XX}} \) | \( -3.69 \times 10^{-03} \) | \( -5.10 \) | \( -3.41 \times 10^{-13} \) | \( 6.66 \times 10^{-16} \) | 10 |

(With about 150 g H₂O) and solid salt mixtures in an environmental chamber (Ecosphere, Despatch) at controlled relative humidity and temperature. Under these conditions the dissolved salt mixture evaporates concentrating the solution and precipitating one of the two salts, and the solid salt mixture absorbs water dissolving the salts until equilibrium is reached.

For each run, four Teflon™ beakers containing the dissolved salts and four beakers containing the solid salts were placed into the chamber and sequential pairs of initially aqueous and initially solid beakers were sampled over time. Figure 6 shows that steady-state relative humidity and solution composition are achieved with in the first 200 h of reaction and that solution composition of initially dissolved and initially solid samples converge over the time period of the experiments. Samples were typically taken every one to three days. Calibrated temperature (±1 °C) and relative humidity probes (Vaisala Inc., model HMP243 or HMP233) were placed just above the solutions in the beakers, because microenvironments within the beakers differed from the environmental chamber relative humidity by as much as 5% relative humidity. Relative humidity probe calibration checks were conducted in saturated KNO₃ solutions from 90 to 110 °C. Statistical analysis of these RH measurements together with vapor pressure measurements for KNO₃ (Ref. 12) yield an average standard deviation of about 1.6 RH units. Uncertainty reported in the tables and figures is calculated as 2σ (3.1% RH units).

FIG. 6. Examples of the brine % relative humidity and composition as a function of time for the reversed deliquescence experiments at 90 °C for (a) NaCl–NaNO₃ and (b) KNO₃–NaNO₃ mixtures.
Samples were taken when there was at least 10 g of solution in each beaker. The exact amount of solution was dependent on relative humidity and solubility of the salt mixture. About 1 g of solution was collected from each beaker and filtered through a 0.45 μm syringe-less filter into a sampling bottle, the bottle was sealed and weighed to determine sample amount, and then diluted with about 250 g of distilled and de-ionized water. All dilution factors were determined gravimetrically. Each time a pair of samples was taken, the temperature and relative humidity probes were moved to monitor the next pair of beakers. Solids from the fourth pair of samples were separated from the remaining solution by filtration (0.45 μm pore size), dried, and stored in a desiccator until analyzed by powder x-ray diffraction.

IV. RESULTS

The deliquescence of NaCl–NaNO₃, KNO₃–NaNO₃, and NaCl–KNO₃ salt mixtures from 90 to 120 °C is summarized in Tables II–VI and in Figs. 1–5. Figures 1 and 2 compare the experimental results of the reversed deliquescence experiments with the model calculations for the NaCl–NaNO₃–H₂O system at 90 and 110 °C. Equilibrium is shown by the convergence of the measured relative humidity and solution composition for the initially dissolved and initially solid salt mixtures. At 90 °C, we also show previous solubility data by Linke, which agrees with our results.
Although there is good agreement between experiment and model for solutions $X_{NO_3} < 0.5$, there are discrepancies for both solution composition and relative humidity for nitrate-rich solutions near the eutonic. The model overpredicts relative humidity by as much as 8% relative humidity and underpredicts the solution composition by as much as 8 molal (or 40%). At 90°C, the experimental data suggest a deliquescence relative humidity of 56% RH ($X_{NO_3} = 0.85$) compared.
TABLE VI. Solution % RH and composition from reversed deliquescence of NaCl–KNO₃ mixtures at 120 °C. Reported values represent the average steady-state solution composition.

| Expt. ID | T (°C) | % RH ±3.1 | Na molal | K molal | Cl molal | NO₃ molal | [Na]/[K] |
|----------|--------|-----------|----------|---------|----------|-----------|---------|
|          |        | Initially dissolved salt |          |         |          |          |         |
| MS-34A(44) | 120    | 43.0       | 8.35±0.00 | 17.19±0.32 | 6.14±0.00 | 20.22±0.05 | 0.33±0.01 |
| MS-34A(44) | 120    | 41.6       | 10.98±0.03 | 27.72±0.06 | 5.95±0.00 | 33.43±0.14 | 0.28±0.01 |
| MS-34A(48) | 120    | 48.1       | 8.18±0.06 | 16.55±0.25 | 6.09±0.02 | 19.27±0.06 | 0.33±0.01 |
| MS-39A    | 119    | 47.3       | 9.14±0.07 | 20.33±0.13 | 6.09±0.04 | 23.85±0.09 | 0.31±0.01 |
| MS-40A    | 119    | 47.9       | 5.54±0.05 | 30.26±0.08 | 5.53±0.00 | 30.38±0.13 | 0.16±0.00 |
| MS-41A    | 119    | 45.7       | 9.86±0.05 | 22.09±0.03 | 6.22±0.02 | 26.44±0.06 | 0.31±0.01 |
| MS-42A    | 119    | 43.8       | 7.35±0.02 | 30.14±0.14 | 5.60±0.00 | 31.62±0.03 | 0.20±0.00 |
| MS-43A    | 119    | 43.3       | 10.65±0.03 | 24.90±0.04 | 6.00±0.03 | 29.29±0.17 | 0.30±0.00 |
| MS-44A(40)| 119    | 41.9       | 8.57±0.01 | 29.30±0.18 | 5.71±0.00 | 32.51±0.03 | 0.23±0.00 |
| MS-44A(41)| 119    | 42.9       | 8.19±0.01 | 29.28±0.09 | 5.45±0.00 | 31.94±0.05 | 0.22±0.00 |
|          |        | Initially solid salt |          |         |          |          |         |
| MS-33B(48)| 120    | 48.7       | 4.64±0.03 | 27.60±0.22 | 4.60±0.03 | 27.94±0.03 | 0.14±0.00 |
| MS-34B(44)| 120    | 45.3       | 9.45±0.09 | 26.16±0.16 | 5.74±0.00 | 30.67±0.07 | 0.27±0.01 |
| MS-34B(41)| 120    | 41.0       | 10.89±0.03 | 28.53±1.11 | 5.92±0.00 | 34.26±0.06 | 0.28±0.01 |
| MS-34B(48)| 119    | 49.0       | 8.11±0.02 | 18.20±0.27 | 5.76±0.02 | 21.47±0.03 | 0.31±0.01 |
| MS-39B    | 119    | 46.9       | 5.30±0.01 | 28.48±0.16 | 5.31±0.02 | 28.50±0.03 | 0.16±0.00 |
| MS-40B    | 119    | 46.2       | 5.84±0.01 | 31.11±0.01 | 5.86±0.00 | 31.62±0.16 | 0.16±0.00 |
| MS-41B    | 119    | 46.1       | 10.02±0.03 | 23.20±0.06 | 6.01±0.02 | 27.25±0.15 | 0.30±0.00 |
| MS-42B    | 119    | 47.3       | 7.37±0.01 | 31.58±0.16 | 5.83±0.00 | 33.11±0.01 | 0.19±0.00 |
| MS-43B    | 120    | 43.6       | 11.24±0.01 | 26.87±0.05 | 6.36±0.01 | 31.73±0.08 | 0.30±0.00 |
| MS-44B(40)| 119    | 41.3       | 9.11±0.05 | 28.91±0.31 | 5.69±0.01 | 32.42±0.02 | 0.24±0.00 |
| MS-44B(41)| 119    | 42.4       | 8.37±0.03 | 29.79±0.51 | 5.72±0.01 | 32.65±0.10 | 0.22±0.00 |

to the model prediction of 59% RH (X(NO₃)=0.92). Similarly at 110 °C, the experimental data suggest a deliquescence relative humidity of 52% RH (X(NO₃)=0.9) compared to the model prediction of 56% RH (X(NO₃)=0.97).

Although there are discrepancies in the absolute RH and solution composition, both experiment and model exhibit similar trends. Relative humidity decreases from a high value near 75% at low X(NO₃) to a minimum near the eutonic point. Above the eutonic point, the relative humidity increases with increasing X(NO₃) as the deliquescence point of pure soda niter is approached. The higher solubility of soda niter generates nitrate concentrations that are substantially higher than the chloride concentrations above X(NO₃)=0.5. Chloride concentrations decrease with increasing X(NO₃), because chloride solubility is limited by the increasing sodium concentrations from dissolving soda niter (the common ion effect).

The solids consisted of halite with trace soda niter below the eutonic and of soda niter with trace halite above the eutonic. Trace amounts of soda niter and halite probably represent residual solution that was trapped in pore spaces during the filtration process when the salts were dried. Halite should be the only solid phase present below the eutonic because the solution is saturated with respect to halite and undersaturated with respect to soda niter. Above the eutonic, soda niter should be the only solid phase present, because the solution is saturated with respect to soda niter and undersaturated with respect to halite. Only at the eutonic, where both minerals are saturated, would one expect to find both halite and soda niter.

Figure 3 compares the experimental results of the reversed deliquescence experiments with the model calculations for the KNO₃–NaNO₃–H₂O system at 90 °C. Similar to the NaCl–NaNO₃–H₂O system, the convergence between the measured relative humidity and solution composition for initially dissolved and initially solid salt mixtures indicates that equilibrium was achieved. However, there is poor agreement between experiment and model for both the relative humidity and solution composition. Experimental relative humidity values are as much as eight percentage points higher than those predicted by the model on the niter side of the eutonic (X(Na)<0.2). Trends in the experimental data indicate that the deliquescence relative humidity of about 42% agrees with the model prediction, but yields a more KNO₃ rich brine (about X(Na)=0.5) than predicted by the model.

A large discrepancy between experiment and model is seen in the solution composition. Dissolved potassium, sodium, and nitrate concentrations follow similar trends as the model predictions, but the absolute concentrations are significantly higher. In the most extreme case, solution compositions are roughly twice the model prediction with experimental sodium=20 molal, potassium=22 molal, and nitrate=42 molal. The high experimental molal concentrations are not an artifact of deriving the values from solution analyses (see Sec. III D). A test of the analytical methodology using highly concentrated solutions showed that analytically and gravimetrically determined values were generally within 4% of each other. The solids consisted of niter with trace soda niter, below the experimental eutonic and of soda niter with trace niter, above the experimental eutonic. Trace amounts of soda niter or niter probably represent residual
solution that was trapped in pore spaces during the filtration process when the salts were dried.

Figures 4 and 5 compare the experimental results of the reversed deliquescence experiments with the model calculations for the NaCl–KNO₃–H₂O system at 90 and 120°C. Similar to the other salt systems studied here, the divergence between the measured relative humidity and solution composition for initially dissolved and initially solid salt mixtures indicates that equilibrium was achieved. Values for the deliquescence relative humidity are in agreement at both temperatures. This agreement at the eutonic relative humidity appears to be fortuitous, because there is poor agreement between experiment and model for relative humidity and all solution composition. The extent of the mismatch is much greater at 120°C than at 90°C. At 90°C, the greatest mismatch occurs in KNO₃-rich solutions where the model underpredicts relative humidity by as much as five percentage points and underpredicts solution composition by as much as 4 molal (about 30%). In solutions dominated by NaCl (X_{Na}>0.5), there is reasonable agreement between model and experiment. At 120°C, the mismatch between experiment and model relative humidity is similar to that at 90°C. However, at this higher temperature, the model significantly underpredicts the solution composition. In the most extreme case, solution compositions are roughly twice the model prediction with experimental sodium=11 molal, potassium=28 molal, chloride=6 molal, and nitrate=33 molal. At 120°C, atmospheric pressure limits the experiments to 50% relative humidity, so we cannot determine if the model adequately predicts relative humidity and solution composition in NaCl-rich solutions.

Analysis of the solids shows that sylvite (KCl) is an important solubility control near the experimental eutonic in agreement with the results of model calculations at these temperatures. At 90°C, niter, sylvite, and minor amounts of halite were detected just to the left of the eutonic (0.28 =X_{Na}=0.31), and halite, sylvite, and minor amounts of niter were detected to the right side of the eutonic (0.35=X_{Na} =0.40). As is expected, the solids consisted of niter (X_{Na} =0.25) and halite (X_{Na}=0.60) on their respective limbs of the phase diagram. At 120°C, solutions were saturated with respect to niter, sylvite, and halite between most of samples between 0.15<X_{Na}>0.30. One sample at X_{Na}=0.14 contained only niter, two samples at X_{Na}=0.16 and X_{Na}=0.30 contained niter and halite, but no sylvite. Any trace amounts of salt detected probably represent residual solution that was trapped in pore spaces during the filtration process when the salts were dried.

V. DISCUSSION

A. Na–Cl, Na–NO₃, and K–NO₃ high-temperature Pitzer models

The comparison of model predictions and experimental results of relative humidity and solution compositions for the NaCl–NaNO₃–H₂O, KNO₃–NaNO₃–H₂O, and the NaCl–KNO₃–H₂O systems from 90 to 120°C indicate that some parameters used in the current high-temperature Pitzer model do not adequately describe brine chemistry formed by deliquescence of these salt mixtures. Before we discuss the specific data needs to resolve discrepancies between experimental results and model predictions, we review the basic high-temperature Pitzer model used in these simulations.⁸

The Pitzer model is derived by first defining an expression for the excess Gibbs free energy (G^{ex}) of the total solution [Ref. 9, Eq. (23)]:

\[
\frac{G^{ex}}{RTw_w} = f(I) + \sum_i \sum_j \lambda_{ij}(I)n_in_j + \sum_i \sum_j \sum_k \mu_{ijk}n_in_jn_k, \tag{8}
\]

where G^{ex} is the difference or “excess” in the Gibbs free energy between a real solution and an ideal solution defined on the molality composition scale, R is the universal gas constant, T is the absolute temperature, w_w is the mass (kg) of solvent water, f is a Debye–Hückel function that depends on the ionic strength (I=\Sigma nm^2z^2), \lambda_{ij} is a second-order interaction coefficient (also a function of I), \mu_{ijk} is a third-order interaction coefficient, n denotes the number of moles of a species, and i, j, and k denote solute species. Here m denotes molality and z the charge number. Note that molality is defined as m_i=n_i/w_w. Upon substitution of m_iw_w for n_i (and so forth for the j and k cases) in Eq. (8), the ionic solute activity coefficient (γ_i) and the solvent osmotic coefficient (ϕ) may be calculated as the partial derivatives with respect to the molality of the ionic solute and the mass of water, respectively:

\[
\ln \gamma_i = \left[ \frac{\partial (G^{ex}/w_wRT)}{\partial m_i} \right]_{w_w}, \tag{9}
\]

\[
\phi - 1 = -\frac{\partial (G^{ex}/\partial w_w)}{RT} \sum_i m_i \tag{10}
\]

[Ref. 9, Eqs. (34) and (35)]. The activity of water is closely related to the osmotic coefficient (ln a_w=−(Σm_i/Ω)ϕ, where Ω is the number of moles of water comprising a 1 kg mass, approximately 55.51).

Substitution of Eq. (8) into Eqs. (9) and (10) followed by differentiation yields the fundamental Pitzer equations for the solute activity coefficient and the osmotic coefficient (or alternative forms for the activity of water or the activity coefficient of water). See BSC⁸ or Pitzer² for full details of the applied forms of the Pitzer equations and the corresponding practical interaction coefficients. Values for the practical interaction coefficients are generally obtained by fitting physical property measurements, such as the osmotic coefficient, the vapor pressure of water over salt solutions, or (less commonly) mineral solubilities.

The model requires only two-ion (β^{(0)}_{MX}, β^{(1)}_{MX}, β^{(2)}_{MX}, C^{φ}_{MX}, S^{θ_{MM'X}} and S^{θ_{XX'}}) and three-ion (ϕ_{MM'X} and ϕ_{MMXX}) interaction parameters in the present study of ionic systems. Here M denotes a cation, M' a different cation, X an anion, and X' a different anion. The S^{θ_{MM'X}}, S^{θ_{XX'}} parameters usually occur in mixtures of aqueous electrolytes (e.g., MX–M'X, MX–MX', or more complex mixtures). Within the framework of the standard Pitzer model, the values of the mixing parameters are independent of the possible presence of other types of ions in the solution, and
once their values have been determined for a particular system, the same values may be used for all other relevant systems.9

The high-temperature Pitzer model8 employed in the present study uses the following equation to represent the temperature dependence of each of these ion interaction parameters:

$$\chi(T) = a_1 + \frac{a_2}{(T - T_r)} + a_3 \ln(T/T_r) + a_4(T - T_r),$$

where $\chi$ represents any of the above-noted practical interaction parameters,13 $T_r$ is the reference temperature (298.15 K), and $a_1$, $a_2$, $a_3$, and $a_4$ are fitted coefficients. A variety of other forms are extant in the literature (e.g., Refs. 10, 14). For the model used here,9 data taken from other models (see the following) were refit as necessary for consistency with the above temperature function. The differences associated with refitting from a different temperature function are negligible within the temperature ranges of the original fits.

Although the high-temperature Pitzer model used in the present study is a fairly comprehensive one accounting for the nonideal behavior of highly concentrated electrolytes over a wide range of temperature (nominally 0–200 °C), there are still significant data needs for common ions. The present model was founded on earlier high-temperature Pitzer models (Refs. 10, 14, and references cited by them), supplemented by parameter data from several other sources.11,15–24 It is also partly based on refitting of parameterizations from the published literature to the most widely used (standard) form of the Pitzer equations.25

The Yucca Mountain Project high-temperature Pitzer model contains robust thermodynamic submodels for the Na–NO$_3$, Na–Cl, K–Cl, Na–K, and K–Na–Cl ion interactions. The Na–NO$_3$ model is based on data from −37 to 152 °C11 that was refit for consistency with the standard Pitzer form. Some degradation in fit quality results from this refitting, increasing the deviation in the osmotic coefficient from about 0.01 to about 0.02.25 Similarly, two-ion and three-ion models in the K–Na–Cl system are based on data from 0 to 300 °C16 fitting the standard Pitzer form. In contrast, the K–NO$_3$ and Cl–NO$_3$ models are based on only 25 °C data9 and there are no parameters for the Na–K–NO$_3$, Na–Cl–NO$_3$, or K–Cl–NO$_3$ ion interactions. Our experimental data in the NaCl–NaNO$_3$–H$_2$O system indicate that temperature dependent parameters for Cl–NO$_3$ and/or Na–Cl–NO$_3$ ion interactions are needed to describe the relative humidity and the solution composition near the eutonic point where maximum solubilities are approached. The absence of temperature dependent parameters for K–NO$_3$ ion interactions in the Yucca Mountain Project high-temperature Pitzer model is the primary cause of the poor prediction of the deliquescence of salt mixtures containing KNO$_3$ at elevated temperatures (Figs. 3–5) as well as the measured % relative humidity and solubility of KNO$_3$ at elevated temperature (Fig. 7). Additionally, some of the mismatch in the NaCl–KNO$_3$–H$_2$O system may also be due to the absence of temperature dependent parameters for Cl–NO$_3$, Na–Cl–NO$_3$, and/or K–Cl–NO$_3$ ion interactions, in addition to the absence of temperature dependent K–NO$_3$ ion interaction parameters.

B. Implications for radioactive waste disposal

It is important that geochemical calculations of the chemical environment at the waste package surfaces use a robust high-temperature Pitzer ion interaction model for common ions, because the deliquescence of aerosol salts and dust is likely to be a primary source of brines that contact the waste containers and drip shields. In addition to the discrepancy identified for relative humidity and solution composition for salt mixtures containing KNO$_3$ stemming from the use of a constant temperature model for K–NO$_3$ interactions, discrepancies for magnesium and ammonium salt mixtures at elevated temperatures are likely because the model includes constant temperature models for many of their respective ion interactions.8 Osmotic and activity coefficients must be experimentally determined as a function of temperature to derive the ion interaction parameters needed to describe the nonideal behavior of these concentrated solutions, because the Pitzer model is empirically based. Of the salt systems listed above, robust models for potassium salts are probably the most important at high temperature, because magnesium
concentrations are likely to be limited by insoluble silicate minerals and ammonium concentrations are likely to be limited by gas volatility.

Recent modeling efforts by the Yucca Mountain Project predict that mixtures of NaCl, KNO$_3$ and/or NaNO$_3$ are the most prevalent mineral assemblages that may deliquesce in repository environments using the current high-temperature Pitzer model. As the temperature increases, the deliquescence relative humidity and the NO$_3^-$ concentrations increase (Fig. 7). We expect only small differences between predicted and actual deliquescence relative humidity and brine composition at temperatures below 60 °C, because the model adequately predicts niter solubility at these temperatures. However, at higher temperatures, much larger differences between predicted and actual environment are expected, because the model underpredicts niter solubility by about 200% at 135 °C [Fig. 7(b)]. At these temperatures the current Pitzer model will significantly underpredict brine NO$_3^-$ brine composition because the K–NO$_3^-$ interactions will be more important. This is clearly illustrated in our KNO$_3$–NaNO$_3$ and NaCl–KNO$_3$ deliquescence experiments, where NO$_3^-$ concentrations can be twice the predicted concentrations. Additionally, it is likely that calculated deliquescence relative humidities for the three salt system are of limited accuracy, because the current model for KNO$_3$ is of limited accuracy at high temperature (Fig. 8). Therefore calculated dry-out or deliquescence temperatures are uncertain. Dry-out or deliquescence temperatures made assuming a total pressure similar to current atmospheric pressure (0.90 bar) predict that a brine saturated with NaCl, NaNO$_3$, and KNO$_3$ would boil just above 135 °C.

VI. CONCLUSIONS

Adsorption of water by deliquescent salt minerals found in aerosols and dusts that may be deposited on waste package surfaces during the construction and ventilation stages of a high-level radioactive waste repository at Yucca Mountain, NV, will be a primary source of brines that might lead to corrosion of the waste package surfaces. Although the deliquescence relative humidity of most pure salt minerals is known over a range of temperature, the behavior of salt mixtures at elevated temperatures is unknown. Our reversed deliquescent experimental results in saturated NaCl–NaNO$_3$–H$_2$O, KNO$_3$–NaNO$_3$–H$_2$O, and NaCl–KNO$_3$–H$_2$O systems from 90 to 120 °C show that use of 25 °C parameter values for K–NO$_3$ and Cl–NO$_3$ (and possibly for three-ion parameters in the Na–K–Cl–NO$_3$ system) in the Yucca Mountain Project high-temperature Pitzer model do not accurately predict the equilibrium solubility and corresponding relative humidity of KNO$_3$ salt mixtures and of NaCl–NaNO$_3$ mixtures near the eutonic composition.

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