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Deliquescence of NaCl-NaNO₃ and KNO₃-NaNO₃ Salt Mixtures at 90°C

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Abstract

We conducted reversed deliquescence experiments in saturated NaCl-NaNO₃-H₂O and KNO₃-NaNO₃-H₂O systems at 90°C to determine 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, USA. Model predictions agree with experimental results for the NaCl-NaNO₃-H₂O system, but underestimate relative humidity by as much as 8% and solution composition by as much as 50% in the KNO₃-NaNO₃-H₂O system.

Key Words

Deliquescence, halite, soda niter, niter, brine

1.0 Introduction

Yucca Mountain, Nevada is the designated geologic repository for permanent disposal of high-level nuclear waste. Current waste package design calls for double walled canisters with an inner wall of 316L stainless steel and an outer wall of highly

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resistant Ni-Cr-Mo alloy, which are covered with grade 7 Ti drip shields to protect the canisters from rock fall and seepage water (Gordon, 2002). 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 canisters and drip shields are those formed by the absorption of water by hygroscopic salts found in local and regional dust entrained 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 100°C at atmospheric pressure. The relative humidity at which salts deliquesce is dependent on temperature and is characteristic to each salt mineral or assemblage of salt minerals. For example at 90°C, MgCl_2 deliquesces at 24% relative humidity and KCl deliquesces at 78.5% relative humidity (Greenspan, 1977). 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 (Ge et al, 1998; Tang and Munkelwitz, 1993, 1994) and single salts at higher temperatures (Greenspan, 1977).

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. BSC (2003a) used the EQ3/6 geochemical code and the high temperature Pitzer ion interaction parameter thermodynamic database to account for non-ideal behavior of the brine solutions 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(s) 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 canister 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 and KNO₃-NaNO₃-H₂O systems at 90°C. These are benchmark experiments that can be used to assess the validity of the model calculations and Pitzer parameters that account for non-ideal ion interactions in these highly concentrated solutions.

2.0 Model Calculations

Relative humidity is thermodynamically tied to solution composition through the activity of water. The activity of water, a_w , is the product of its mole fraction of water, X_w , and its mole fraction activity coefficient, γ_w :

$$a_w = X_w \gamma_w \quad 1.$$

The mole fraction of water is dependent on the solution composition:

$$X_w = n_w / (n_w + \sum n_i) \quad 2.$$

where n_w and n_i are the number of moles of water and of dissolved constituent i , respectively. The concentrations of the dissolved constituents are limited by the solubilities of the thermodynamically stable salt minerals. If we use halite (NaCl) as an example, then the solubility product, K_{NaCl} , at a given temperature is dependent on the Na^+ and Cl^- concentrations and activity coefficients according to the mass balance reaction:



$$K_{\text{NaCl}} = (m_{\text{Na}^+} \gamma_{\text{Na}^+})(m_{\text{Cl}^-} \gamma_{\text{Cl}^-}) \quad 3b$$

where m_i and γ_i indicate the molality and activity coefficient of species i .

Relative humidity, RH_{frac} , is related to activity of water through the partial pressure of water vapor, and is equivalent to:

$$RH_{\text{frac}} = p_w / p_w^o \quad 4.$$

where p_w is the partial pressure of water vapor over an aqueous solution and p_w^o is the partial pressure of water vapor in the standard state over pure water. Similarly, the activity of water is equivalent to:

$$a_w = f_w / f_w^o \quad 5.$$

where f_w is the fugacity of water vapor over an aqueous solution and f_w^o is the fugacity of water vapor in the standard state over pure water. Equating fugacity with its partial pressure:

$$f_w / f_w^o = p_w / p_w^o \quad 6.$$

yields:

$$RH_{frac} = a_w \quad 7.$$

The activity of water is commonly expressed in decimal form, the RH commonly 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 $p_w = p_w^o a_w$, and increases 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.

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 and 2 show the model calculations of relative humidity and solution composition at 90°C versus X_{NO_3} and X_{Na} for the NaCl-NaNO₃-H₂O and the KNO₃-NaNO₃-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 eutectic 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 eutectic point

is reached. An identical approach is used for the $\text{KNO}_3\text{-NaNO}_3\text{-H}_2\text{O}$ system. We use EQ3/6 geochemical code (Wolery and Jarek, 2003) and a high temperature Pitzer ion interaction thermodynamic data base (BSC, 2003b; Pitzer, 1991; Rard and Wijesinghe, 2003) 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 ($\beta_{M,X}^{(0)}$, $\beta_{M,X}^{(1)}$, $\beta_{M,X}^{(2)}$, $C_{M,X}^\phi$) between two different kinds of ions of opposite charge (cation M and anion X), and also binary ($\theta_{M,M'}$, $\theta_{X,X'}$) interactions between ions of like charge and ternary interactions ($\psi_{M,M',X}$, $\psi_{X,X',M}$) involving three ions in common-cation and common-anion ternary systems.

3.0 Experimental Methods

3.1. Starting Materials

Analytical grade sodium chloride (NaCl), sodium nitrate (NaNO_3), and potassium nitrate (KNO_3) were used to synthesize dissolved and dry salt mixtures. Distilled and deionized (18 M-ohm) water was used to make all solutions.

3.2. Reverse Deliquescence Experiments

We measured brine composition at controlled relative humidity and 90°C for NaCl- NaNO_3 and $\text{KNO}_3\text{-NaNO}_3$ salt mixtures as a function of X_{NO_3} and X_{Na} , respectively. 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 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 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 3 shows that steady-state relative humidity and solution composition are achieved for both salt systems within the first 200 hours 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 ($\pm 0.05^{\circ}\text{C}$) and relative humidity ($\pm 2.0\%$)² probes 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. About one gram of solution was collected from each beaker and filtered through a 0.45μ syringe-less filter into a sampling bottle, the bottle was sealed and weighed to determine sample amount, and then diluted with about 250 grams of distilled and deionized 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 of the fourth pair of samples were separated from the remaining solution by filtration (0.45μ pore size), dried, and stored in a desiccator until analyzed by powder X-ray diffraction

3.3. *Analytical Techniques*

² Relative humidity probes are calibrated at three temperatures (20, 40 and 60°C) and three relative humidities (15, 50, and 85 %RH) using a two pressure system for humidity standards. We assume that this

All aqueous samples were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) for sodium, and by ion chromatography (IC) for chloride, nitrate, potassium, and sodium for some samples. Analytical uncertainty for the ICP-AES and the IC is less than 2%. Solids were analyzed using powder X-ray diffraction (XRD) for detection of halite, soda niter, and niter.

3.4. *Calculation of Molal Concentrations*

Solution compositions were converted from mg/kg-solution to molality (mol/kg-solvent) by subtracting the weight of the dissolved constituents from the sample weight to calculate the weight of solvent water. We used this method to calculate the molality of several independently determined solutions ranging from 5 to 35 molal at 90 to 105°C to assess the uncertainty of this method. Molality and X_{Na} derived from solution analyses are generally within 4% and 1% of their respective gravimetric determinations, which agrees with uncertainty of the averaged values reported in Tables 1 and 2.

4.0 Results

The deliquescence of NaCl-NaNO₃ and KNO₃-NaNO₃ salt mixtures at 90°C are summarized in Tables 1 and 2 and in Figures 1 and 2. Figure 1 compares the experimental results of the reversed deliquescence experiments with the model calculations for the NaCl-NaNO₃-H₂O system at 90°C. Equilibrium is shown by the convergence of the measured relative humidity and solution composition for the initially dissolved and initially solid salt mixtures. There is good agreement between experiment

calibration is valid at 90°C.

and model for both the relative humidity and solution composition. Model predictions of relative humidity are within (or slightly lower than) the accuracy of the experimental values. Model predictions of solution composition agree with experiment, with the exception of slightly lower experimental sodium and nitrate concentrations for one sample at $X_{\text{NO}_3} = 0.85$.

As predicted by the equilibrium model, the relative humidity decreases from a high value near 75% at low X_{NO_3} to a minimum near the eutectic point. Above the eutectic point, the relative humidity increases with increasing X_{NO_3} as the deliquescence point of pure soda niter is approached. In agreement with the model predictions, the higher solubility of soda niter generates nitrate concentrations that are substantially higher than the chloride concentrations above $X_{\text{NO}_3} = 0.5$. Chloride concentrations decrease with increasing X_{NO_3} , 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 eutectic and of soda niter with trace halite above the eutectic. These results agree with model predictions. 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 eutectic because the solution is saturated with respect to halite and undersaturated with respect to soda niter. Above the eutectic, 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 eutectic, where both minerals are saturated, would one expect to find both halite and soda niter.

Figure 2 compares the experimental results of the reversed deliquescence experiments with the model calculations for the $\text{KNO}_3\text{-NaNO}_3\text{-H}_2\text{O}$ system at 90°C . Similar to the $\text{NaCl-NaNO}_3\text{-H}_2\text{O}$ 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 8 percentage points higher than those predicted by the model on the niter side of the eutectic ($X_{\text{Na}} < 0.2$). Trends in the experimental data indicate that the deliquescence relative humidity is only slightly higher than the model prediction (about 42%), but yields a more KNO_3 rich brine (about $X_{\text{Na}} 0.5$) 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 section 3.4). Comparison of molal concentrations determined analytically and gravimetrically yielded values that were generally within 4% of each other. The solids consisted of niter with trace soda niter, below the experimental eutectic and of soda niter with trace niter, above the experimental eutectic. 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.

5.0 Discussion

5.1 *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 and the KNO₃-NaNO₃-H₂O systems at 90°C indicate that the current high-temperature Pitzer model adequately describes brine chemistry formed by the deliquescence of halite and soda niter, but that this same model falls short of describing the deliquescence of the niter and soda niter mixtures. Before we discuss the specific data holes for the K-Na-NO₃ ion interactions we review the basic high temperature Pitzer model that was used in these simulations (BSC, 2003b).

The Pitzer's model is thermodynamically defined by the excess Gibbs free energy (G^{EX}) of the total solution (Pitzer 1991):

$$G^{\text{EX}}/w_w = RT \sum_i m_i (1 - \phi + \ln \gamma_i) \quad 8.$$

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, w_w is the mass of water in the solution in kilograms, m_i is the molality of the i th type of ion, ϕ is the molality based osmotic coefficient of the solvent, and γ_i is the molality based activity coefficient of the i th type of ion. R is the universal gas constant and T is the absolute temperature. The solvent osmotic coefficient and ionic solute activity coefficient may be calculated as the partial derivatives with respect to the mass of water and the molality of the ionic solute, respectively:

$$\phi = 1 - [\{\partial G^{\text{EX}}/RT \sum_i m_i\}/\partial w_w]_{n_i} \quad 9.$$

$$\ln \gamma_i = [\partial \{G^{\text{EX}}/RT w_w\}/\partial m_i]_{n_w} \quad 10.$$

Both the osmotic coefficient and the activity coefficient are then empirically derived from experiment in terms of two ion ($\beta_{\text{MX}}^{(0)}$, $\beta_{\text{MX}}^{(1)}$, $\beta_{\text{MX}}^{(2)}$ if needed, C_{MX}^ϕ , ${}^s\theta_{\text{MM}'}$ and ${}^s\theta_{\text{XX}'}$) and three-ion ($\psi_{\text{MM}'\text{X}}$ and $\psi_{\text{MXX}'}$) interaction parameters that account for the short-range order of complex solutions. Details of the exact form of these virial equations can be found in (BSC, 2003b). The following equation is then used to derive temperature dependence of each of these ion interaction parameters from the experimental data:

$$\chi = a_0 + \frac{a_1}{(T - T_r)} + a_2 \ln(T / T_r) + a_3(T - T_r) + a_4(T^2 - T_r^2) \quad 11.$$

where T_r is the reference temperature (298.15K). Within the framework of this 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 (Pitzer 1991).

Although, the Yucca Mountain Project high temperature Pitzer ion interaction parameter data base represents the most comprehensive data base available to account for the non-ideal behavior of highly concentrated electrolytes over a wide range of temperature (0 to 200°C), there are still significant data gaps for common ions. The database was founded on the original variable-temperature Pitzer parameters (Møller, 1988; Greenberg and Møller, 1989, and references cited by them), supplemented by parameter data from several other sources (Holmes et al., 1987; Pabalan and Pitzer, 1987; Clegg and Brimblecombe, 1990a,b; Thiessen and Simonson, 1990; He and Morse, 1993;

Felmy et al. 1994; Clegg et al 1996; Holmes and Mesmer, 1998; Archer, 2000; Oakes et al., 2000). It also includes thermodynamic parameters converted from non-standard Pitzer equations from the published literature (Rard and Wijesinghe, 2003).

The Yucca Mountain Project high temperature Pitzer ion interaction database contains robust thermodynamic models for the Na-NO₃ and Na-Cl interactions, but the K-NO₃ model is inadequate. The Na-NO₃ model is based on data from -37 to 152°C (Archer 2000) that was refit using the standard Pitzer form. Similarly, the Na-Cl model is based on data from 0 to 300°C (Pitzer et al., 1984; Møller 1988) fit using the standard Pitzer form. In contrast to the Na-NO₃ and Na-Cl models, the K-NO₃ model is based on only 25°C data (Pitzer 1991). Thus the Yucca Mountain Project high temperature Pitzer ion interaction data base does not accurately predict the deliquescence of salt mixtures containing KNO₃ at elevated temperatures (Figure 2) as well as the measured % relative humidity and solubility of KNO₃ at elevated temperature (Figure 4).

5.2 *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 data base for common ions, because the deliquescence of aerosol salts and dust is likely to be a primary source of brines that contact repository canisters and drip shields. In addition to the discrepancy identified for NaNO₃-KNO₃ relative humidity and composition stemming from the use of a constant temperature model for K - NO₃ interactions, discrepancies for other potassium, magnesium, and ammonium salt mixtures at elevated temperatures are likely, because the data base includes constant temperature models for many of their respective ion interactions (BSC 2003b). Osmotic and activity coefficients must be

experimentally determined as a function of temperature to derive the ion interaction parameters needed to describe the non-ideal behavior of these concentrated solutions, because the Pitzer model is empirically based. They cannot be derived from the reversed deliquescence experiments shown here. 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, KNO₃ and/or NaNO₃ are the most prevalent mineral assemblages that may deliquesce in repository environments using the current high temperature Pitzer ion interaction parameter data base (BSC 2003a). As the temperature increases, the deliquescence relative humidity and the NO₃ concentrations increase (Figure 5). 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 constant temperature model underpredicts niter solubility by about 200% at 135°C (Figure 4b). At these temperatures the current Pitzer model will significantly under predict brine NO₃ brine composition because the K-NO₃ interactions will be more important. This is clearly illustrated in our KNO₃-NaNO₃ deliquescence experiments at 90°C, where NO₃ concentrations are about 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 KNO₃ is

of limited accuracy at high temperature (Figure 4a). 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, NaNO₃, and KNO₃ would boil just above 135°C (BSC 2003a).

Although the under prediction of brine chemistry is significant, we do not expect these brines to have a deleterious effect on waste package performance. Current waste package design for the disposal of high-level radioactive waste in the designated repository in Yucca Mountain, Nevada, USA calls for a Ni-Cr-Mo alloy as the outer barrier of the waste canisters and a titanium drip shield, because these materials are highly resistant in most solutions. Solutions that tend to induce corrosion on these materials have high calcium chloride, magnesium chloride concentrations and fluoride concentrations (Gordon, 2002). Although only a few corrosion experiments in highly concentrated brines representative of dust deliquescence have been conducted, nitrate is not considered to be corrosive and has been shown to inhibit localized corrosion in high chloride solutions (Kehler et al., 2001; Dunn and Brossia, 2002; Dunn et al., 2003; BSC, 2003c).

6.0 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, USA 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-NaNO₃-H₂O and KNO₃-NaNO₃-H₂O systems at 90°C show that relative humidity and solution composition for NaCl-NaNO₃-H₂O mixtures at 90°C can be adequately predicted by EQ3/6 geochemical code and the Yucca Mountain Project high-temperature Pitzer ion interaction thermodynamic data base. However, this same data base does not accurately predict experimental relative humidity and solution compositions for the KNO₃-NaNO₃-H₂O system because K-NO₃ ion parameter model is a constant temperature model based only on 25°C data.

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Table 1. Solution %RH and composition from reversed deliquescence of NaCl-NaNO₃ mixtures at 90°C. Reported values represent the average steady-state solution composition.

Exper. ID	T °C	%RH ±1.5	Na molal	Cl molal	NO ₃ molal	X _{NO₃}
Initially Dissolved Salt						
MS-9A	91	75	7.44±0.01	6.60±0.03	0.85±0.00	0.114±0.000
MS-10A	90	69	9.70±0.16	5.29±0.01	4.50±0.02	0.460±0.001
MS-11A	90	58	19.09±0.09	1.83±0.00	17.30±0.01	0.905±0.002
MS-12A	90	60	16.74±0.98	3.56±0.27	13.31±0.62	0.789±0.005
MS-13A	90	56	18.14±0.41	2.79±0.10	15.10±0.13	0.844±0.003
Initially Solid Salt						
MS-9B	91	75	7.74±0.02	6.48±0.00	1.27±0.00	0.164±0.000
MS-10B	91	69	9.75±0.25	4.86±0.10	4.86±0.12	0.500±0.001
MS-11B	91	58	19.20±0.06	1.87±0.00	17.68±0.08	0.904±0.017
MS-12B	91	59	16.59±0.12	3.39±0.08	13.54±0.08	0.799±0.005
MS-13B	91	56	18.70±0.48	2.84±0.03	15.73±0.18	0.847±0.000

Table 2. Solution % RH and composition from reversed deliquescence of NaNO₃-KNO₃ mixtures at 90°C. Reported values represent the average steady-state solution composition, unless otherwise noted.

Exper. ID	T °C	%RH ±1.5	Na molal	K molal	NO ₃ molal	X _{Na}
Initially Dissolved Salt						
MS-14A1	90	66	3.35±0.01	18.15±0.04	22.02±0.076	0.156±0.004
MS-14A	90	68	1.44±0.39	18.27±0.13	20.40±0.12	0.073±0.019
MS-15A	90	59	18.81±0.10	1.01±0.04	20.23±0.64	0.949±0.002
MS-16A	90	56	20.36±0.95	2.54±0.26	23.02±0.90	0.889±0.006
MS-17A	90	56	10.77±0.59	19.67±1.47	31.04±2.52	0.354±0.005
MS-18A	90	50	14.84±0.41	20.16±0.36	35.47±0.86	0.424±0.002
MS-19A	90	51	21.40±0.26	9.00±0.50	30.89±0.80	0.704±0.011
MS-20A	90	45	18.67±0.27	21.65±0.72	40.24±0.68	0.463±0.009
MS-21A	90	46	22.82±0.98	16.43±0.42	39.17±1.36	0.581±0.006
Initially Solid Salt						
MS-14B	90	67	2.36±0.17	17.93±0.63	20.82±0.63	0.116±0.004
MS-15B	90	58	18.53±0.79	1.12±0.23	20.47±1.32	0.943±0.009
MS-16B	90	55	20.32±0.98	3.33±0.30	23.36±0.73	0.860±0.005
MS-17B3	90	55	10.94±0.00	18.58±0.33	30.01±0.03	0.371±0.006
MS-18B3	90	50	14.44±0.05	19.72±0.05	33.66±0.02	0.423±0.006
MS-19B	90	51	21.66±0.60	9.80±0.90	31.84±0.66	0.689±0.023
MS-20B	90	46	19.71±0.46	22.53±0.40	42.48±0.71	0.467±0.007
MS-21B	90	46	22.54±0.58	16.37±0.15	38.95±0.94	0.579±0.007

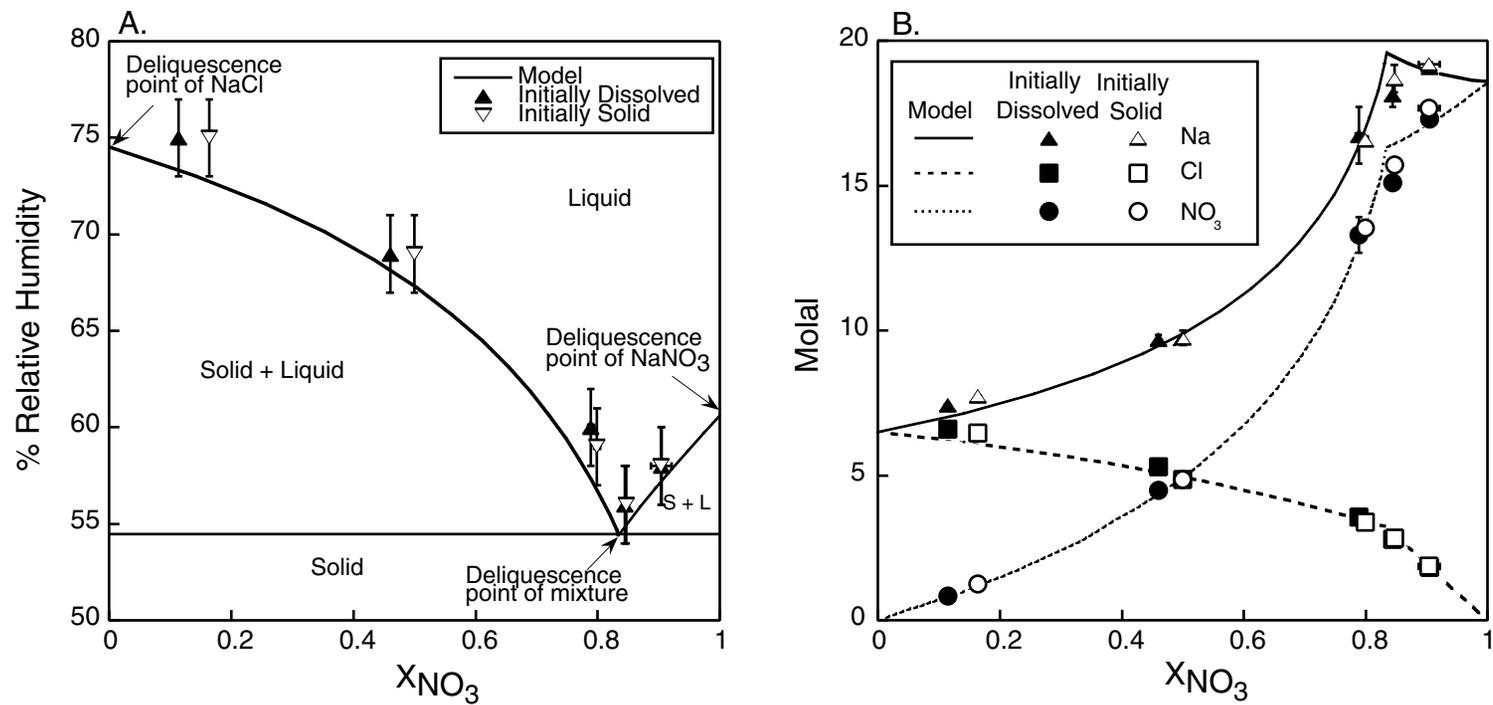


Figure 1. Deliquescence of NaCl-NaNO₃ salts starting from initially dissolved and initially solid mixtures plotted as (A) % relative humidity and (B) solution composition vs X_{NO_3}

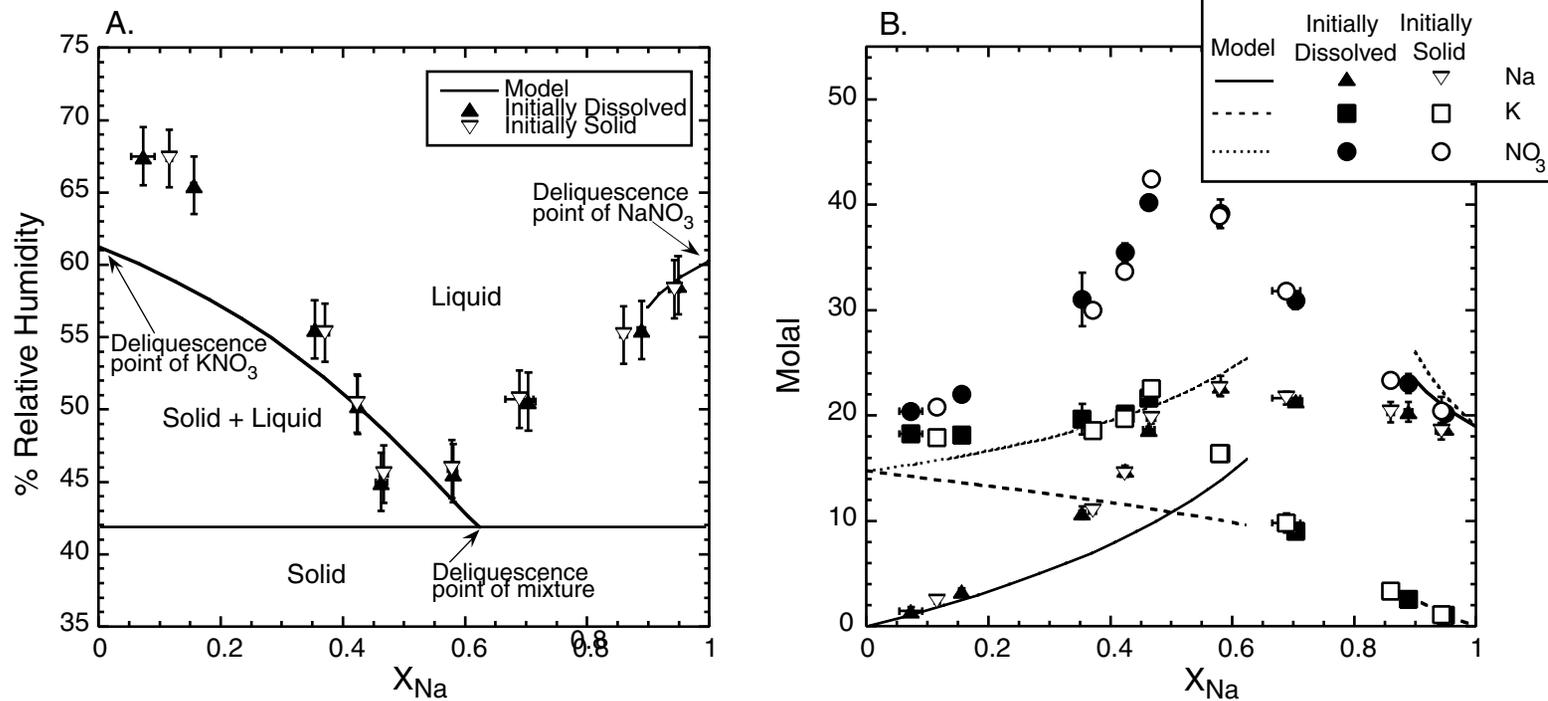


Figure 2. Deliquescence of KNO_3 - NaNO_3 salts starting from initially dissolved and initially solid mixtures plotted as (A) % relative humidity and (B) solution composition vs X_{Na} . The break inlines shows where the model calculations did not converge.

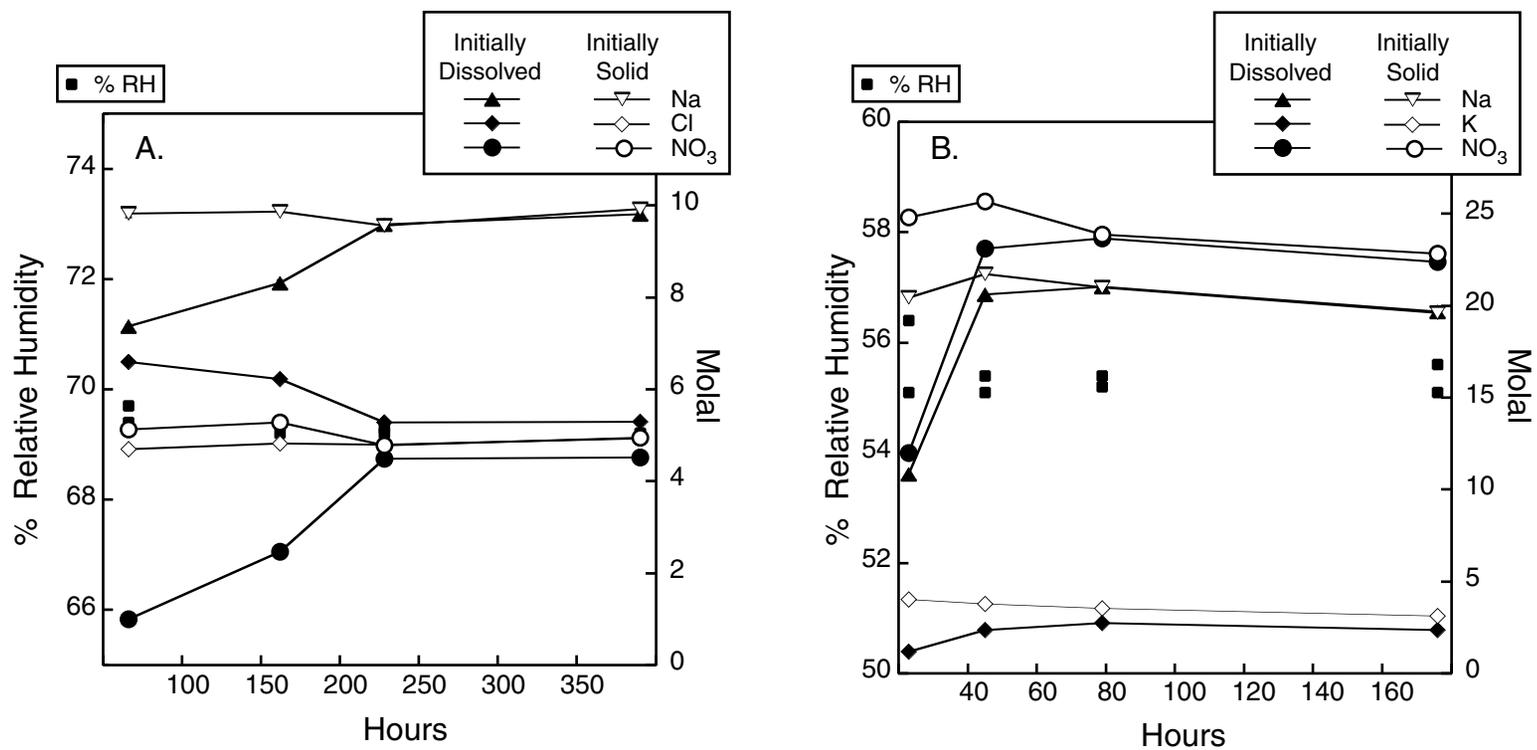


Figure 3. Examples of the % relative humidity and composition as a function of time for the reversed deliquescence experiments at 90°C for (A) NaCl-NaNO₃ and (B) KNO₃-NaNO₃ mixtures.

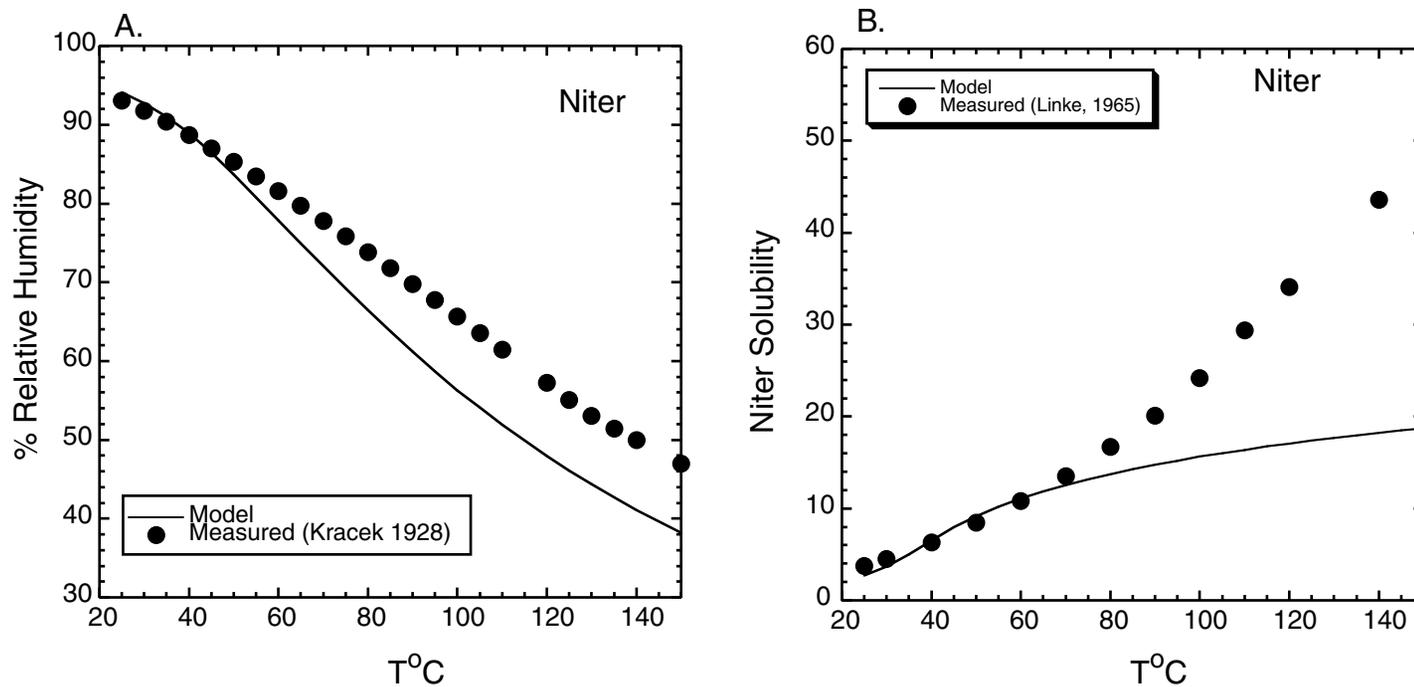


Figure 4. Comparison of predicted and measured niter (KNO₃) (A) % relative humidity and (B) solubility as a function of temperature. Predictions were made using EQ3/6 version 8 geochemical code and the Yucca Mountain high temperature Pitzer ion interaction thermodynamic data base (BSC 2003a,b).

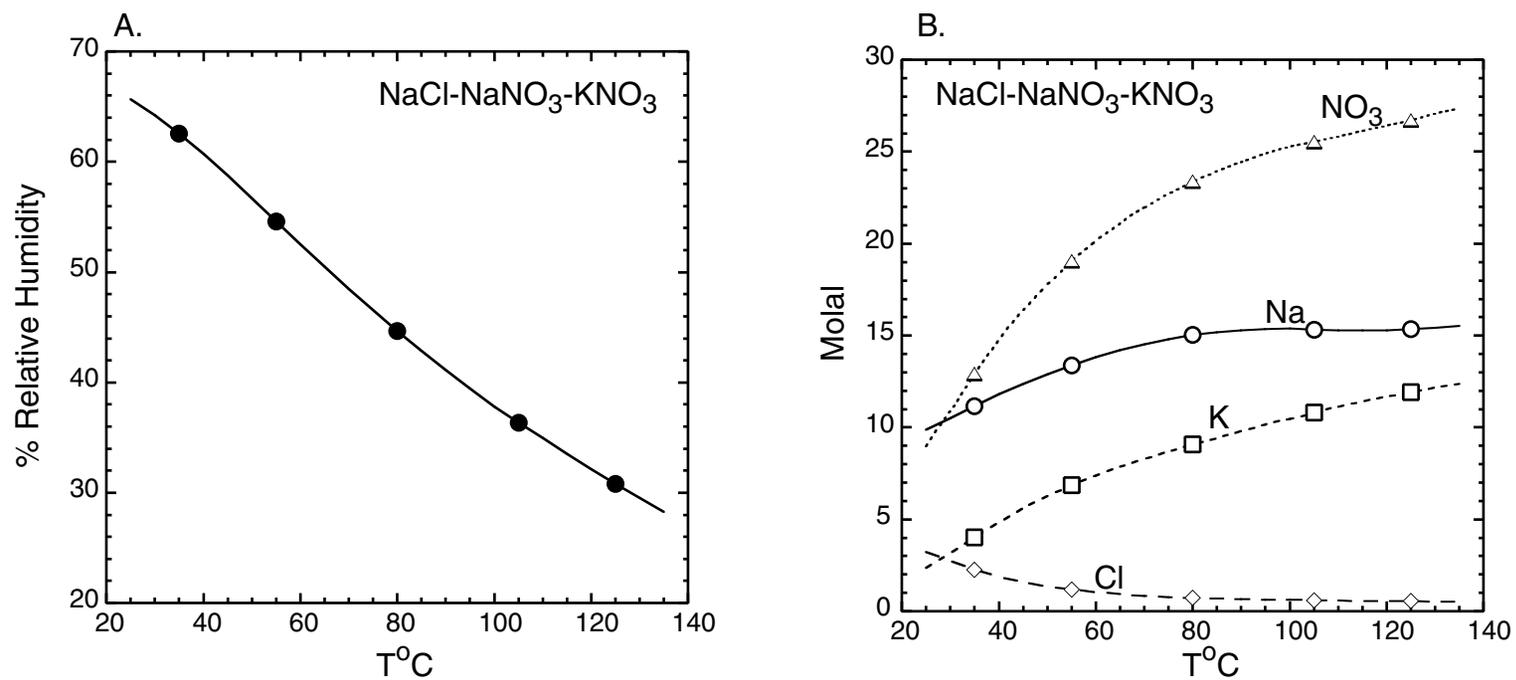


Figure 5. Model predictions of brine (A) % relative humidity and (B) solution composition as a function of temperature at the deliquescence point for a NaCl-NaNO₃-KNO₃ mineral assemblage (BSC 2003b). Predictions were made with EQ3/6 geochemical code and the high temperature Pitzer ion interaction thermodynamic data base. Triangles, circles, squares, and diamonds represent NO₃, Na, K, and Cl concentrations.