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Brines formed by multi-salt deliquescence

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CONTENTS

1. Introduction.....	1
2. Can multi-salt deliquescent brines form at elevated temperature?	2
2.1. Boiling Point Experiments.....	3
2.1.1. Methods.....	3
2.1.2. Results and Discussion	4
2.2. Mutual deliquescence and efflorescence relative humidity experiments	5
2.2.1. Methods.....	6
2.2.2. Results and Discussion	6
2.3. Implications for corrosion at elevated temperatures.....	9
2.4. Bi-thermal Calibration of Relative Humidity Probes	11
3. If brines form at elevated temperature will they persist?.....	16
3.1. Stability of NaCl-KNO ₃ -NaNO ₃ and NaCl-KNO ₃ -NaNO ₃ -Ca(NO ₃) ₂ Brines....	16
3.2. Stability of Ammonium Salts.....	17
4. If brines persist will they be corrosive?	18
4.1. Solubility of NaCl-KNO ₃ -NaNO ₃ salt mixture at 120°C.....	18
4.1.1. Methods.....	18
4.1.2. Results and Discussion	19
5. Conclusions.....	20
6. References.....	21

ABSTRACT

The FY05 Waste Package Environment testing program at Lawrence Livermore National Laboratory focused on determining the temperature, relative humidity, and solution compositions of brines formed due to the deliquescence of NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ salt mixtures. Understanding the physical and chemical behavior of these brines is important because they define conditions under which brines may react with waste canister surfaces. Boiling point experiments show that NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ salt mixtures form brines that transform to hydrous melts that do not truly “dry out” until temperatures exceed 300 and 400°C, respectively. Thus a conducting solution is present for these salt assemblages over the thermal history of the repository. The corresponding brines form at lower relative humidity at higher temperatures. The NaCl-KNO₃-NaNO₃ salt mixture has a mutual deliquescence relative humidity (MDRH) of 25.9% at 120°C and 10.8% at 180°C. Similarly, the KNO₃-NaNO₃ salt mixture has MDRH of 26.4% at 120°C and 20.0% at 150°C. The KNO₃-NaNO₃ salt mixture salts also absorb some water (but do not appear to deliquesce) at 180°C and thus may also contribute to the transfer of electrons at interface between dust and the waste package surface. There is no experimental evidence to suggest that these brines will degas and form less deliquescent salt assemblages. Ammonium present in atmospheric and tunnel dust (as the chloride, nitrate, or sulfate) will readily decompose in the initial heating phase of the repository, and will affect subsequent behavior of the remaining salt mixture only through the removal of a stoichiometric equivalent of one or more anions. Although K-Na-NO₃-Cl brines form at high temperature and low relative humidity, these brines are dominated by nitrate, which is known to inhibit corrosion at lower temperature. Nitrate to chloride ratios of the NaCl-KNO₃-NaNO₃ salt mixture are about NO₃:Cl = 19:1. The role of nitrate on corrosion at higher temperatures is addressed in a companion report (Dixit et al., 2005).

1. 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 containers with an inner wall of stainless steel and an outer wall of highly corrosion resistant Ni-Cr-Mo alloy, which are protected with overlying Ti shields to prevent rocks and seepage water from contacting the containers (Gordon et al., 2005). 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 potential source of brines that may corrode metal containers and drip shields is the absorption of water by hygroscopic salts found in local and regional dust deposited on metal surfaces during the 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. The range of brines formed by the deliquescence of hygroscopic salts found in dusts can

be calculated from mixtures of the pure solid phases using equilibrium thermodynamics, because relative humidity is related to the activity of water and solution composition of corresponding saturated solutions. Wolery (BSC 2004a) 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, NaNO₃ and/or Ca(NO₃)₂ are the most prevalent mineral assemblages. Preliminary results from FY04, showed that three salt mixtures of NaCl, KNO₃, and NaNO₃ produced brines at temperatures exceeding 190°C (Carroll et al, 2005a; Rard 2004). This discovery raised the concern for corrosion in the first 1000 – 2000 years well above 160°C in brine compositions for which corrosion had not been previously investigated.

The *Analysis of Dust Deliquescence for FEP Screening* report addresses the likely-hood of Alloy 22 localized corrosion utilizing the following decision tree (BSC 2005a).

1. Can multi-salt deliquescent brines form at elevated temperatures?
2. If brines form at elevated temperature, will they persist?
3. If brines persist, will they be corrosive?
4. If potentially corrosive brines form, will they initiate localized corrosion?
5. Once initiated, will localized corrosion penetrate the waste package outer barrier?

This is a multi-layered argument in which answers to all of the questions must be yes in order for dust deliquescence to compromise the waste canister surface.

Here we report new experimental data that can be used to help answer the first three questions on the formation, persistence, and corrosiveness of deliquescent brines. The FY05 Waste Package Environment testing program at Lawrence Livermore National Laboratory focused on determining the relative humidity, temperature, and solution compositions of brines formed due to the deliquescence of NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ salt mixtures. We determined the mutual deliquescence relative humidity from 120 to 180°C using resistivity techniques, brine dryout by measuring the maximum boiling point, and brine chemistry from reversed solubility experiments. A subsequent report on corrosion and passive film stability provides new experimental data relevant to the final two questions of the decision tree on the initiation and penetration of localized corrosion (Dixit et al., 2005).

2. Can multi-salt deliquescent brines form at elevated temperature?

Our experiments show that NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ salt mixtures deliquesce at elevated temperature and low relative humidity. In this section we discuss boiling point measurements of brine dryout that show NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ brines form will above 200°C. Complementary mutual deliquescence relative humidity experiments show that NaCl-KNO₃-NaNO₃ brines at temperatures as high as 180°C and RH as low as 10%. In this section, we also discuss the bi-thermal apparatus used to calibrate the relative humidity probes, because accurate measure of the mutual deliquescence relative humidity requires calibration of the relative humidity probes from 120 to 180°C (Carroll et al., 2005b). Source data can be found in

DTN LL050903412251.150 (resistivity experiments), LL050901931032.009 (boiling point experiments), and LL050800623121.053 (reversed solubility experiments).

2.1. Boiling Point Experiments

Boiling temperature measurements were made to directly establish the maximum temperatures at which deliquescence can occur in the following salt systems: NaCl-NaNO₃-KNO₃, NaCl-Ca(NO₃)₂, and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂. This work builds on work reported in FY04 on dryout of NaCl-KNO₃ brines (Rard, 2004). These salt systems were studied because they are predicted to be the ones that determine the brines formed by the deliquescence of salts in dusts at the waste package surface (BSC 2004a, Sections 6.7.2.10 and 6.7.2.13). It is important to make these measurements because the temperature-dependent K-NO₃ and Cl-NO₃ solution Pitzer parameters needed for improving the thermodynamic modeling predictions are not likely to be available in the near future. These measurements will also provide checks on the reliability of future geochemical modeling calculations. Details of the methods and results are available in Rard (2005); the data are contained in DTN: LL050901931032.009.

2.1.1. Methods

The boiling temperature apparatus was described by Rard (2004). Boiling point measurements were made in a 1-liter glass apparatus fitted with a water-cooled condenser column to reduce loss of water during the experiments. The bottom section of the apparatus was inserted into a heating mantle, with heat being applied both to the bottom and to the sides of the apparatus. Salt solutions were stirred and temperature was measured at two different depths to check for adequate mixing. Both the NaCl-Ca(NO₃)₂ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ experiments were performed in which the temperature was recorded when the boiling solutions first took on a slightly opaque/turbid appearance. The initially liquid solutions were heated to evaporate solvent until they became slightly opaque (turbid). This corresponds to the beginning of precipitation of solid phases, and the reported mole fractions at this point should correspond closely to the solution composition.

Two thermocouples were present in the solutions for the boiling temperature measurements. The first thermocouple probe was positioned in the solution near the edge of the flask outside the sweep of the propellers of the stirrer. The second thermocouple probe was inserted into the solution near the center of the flask and above the sweep of the propellers of the stirrer. Type T thermocouples coated with Teflon were used in the majority of the experiments. However, the temperatures encountered for the NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ brines system generally exceed 300°C, and the Teflon coating of the thermocouples melts above 350°C. These two thermocouples were replaced by Type T thermocouples contained in uncoated inconel wells for the remaining NaCl-KNO₃-NaNO₃ experiments. All four thermocouples were calibrated by Heusser Neweigh before, and by Bechtel Nevada after, the boiling temperature measurements were made. The thermocouples were interfaced with a Beamex Multifunctional Calibrator # 009215 or an ΩEOMEGA 450ATT Hand Held Reader.

Based on observations given in the previous report (Rard, 2004), the temperature readings from the second thermocouple probe, which is located near the center of the boiling temperature apparatus, are less affected by the temperature gradient between the

heating mantle and the solution being investigated. Corrected temperatures were based on the readings of this second probe, but were adjusted slightly to bring the measured boiling temperatures for water into agreement with steam table values (Weast et al., 1987, p. D-189 to D-191).

2.1.2. Results and Discussion

The behavior of NaCl-KNO₃-NaNO₃ brine appears to involve a smooth transition from a brine to a hydrous melt near 220°C before it becomes effectively dry by 300°C. There is no phase change associated with the brine-melt “transition,” only a change in preferred terminology. The boiling temperature of this solution gradually increased as more solid dissolved. Between about 200 and 260°C little solid remained, but the solution was opaque (turbid) and boiling vigorously. As the temperature was further increased the rate of boiling decreased and the solution gradually became clear. By 300°C the boiling ceased and did not reoccur as the solution temperature was further increased. A repeat experiment with very nearly the same composition gave a very similar temperature of 297°C when boiling ceased. We assume that the transition between brine solution and hydrous melt occurs at about 220°C because anhydrous NaCl-KNO₃-NaNO₃ mixture has a melting/freezing temperature of $218 \pm 3^\circ\text{C}$ (Rard, 2005). Rard (2004) reported boiling temperatures results for saturated NaCl-KNO₃-NaNO₃ similar NaNO₃/KNO₃ ratio (0.313/0.367) and with variable mole fractions of NaCl. The boiling temperatures ranged from 154°C to 196°C for $x(\text{NaCl}) = 0$ to 0.2299 and increased as the mole fraction of NaCl was increased. Boiling points for select composition of salts added in the NaCl-KNO₃ and KNO₃-NaNO₃ systems were repeated in FY05 and show good agreement with previous results from FY04 (Figure 2.1).

Boiling temperatures for the NaCl-Ca(NO₃)₂ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ solutions are shown in Figure 2.1. The eutectic (maximum boiling temperature) composition for saturated solutions in the NaCl-Ca(NO₃)₂ system occurs at $x\{\text{NaCl}\} \approx 0.25$ and $x\{\text{Ca}(\text{NO}_3)_2\} \approx 0.75$ with a maximum boiling temperature of $164.7 \pm 0.6^\circ\text{C}$. Addition of potassium and sodium nitrate salts produces brine that is stable to much higher temperatures. The dryout temperatures increase rapidly with increasing $x\{\text{Ca}(\text{NO}_3)_2\}$, from $x\{\text{Ca}(\text{NO}_3)_2\} = 0$ to 0.1500. The dryout temperature for the mixtures with $x\{\text{Ca}(\text{NO}_3)_2\} = 0.2000$ and 0.2500 are even higher, $> 400^\circ\text{C}$, but the exact dryout temperatures could not be determined because they exceed the upper limit of our temperature measuring system. However, boiling was extremely slow for these solutions at 400°C, so the dryout temperatures are probably not much higher than this. It should be noted that because the solutions at the dryout temperatures are molten salts, the mole fractions of the solute components will be identical to those calculated from the masses of added salt.

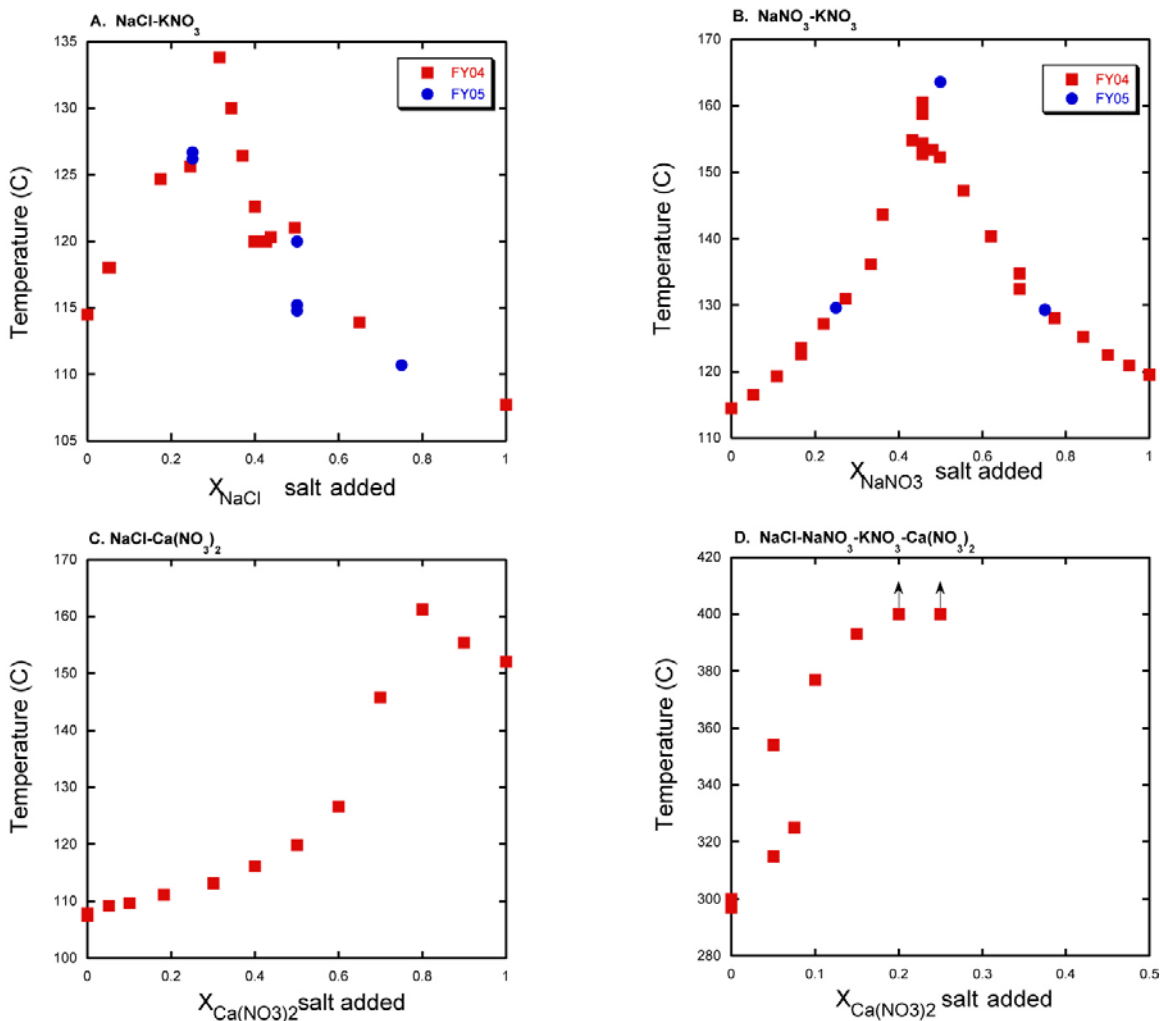


Figure 2.1. Boiling points determined for the (A) NaCl-KNO₃, (B) KNO₃-NaNO₃, (C) the NaCl-Ca(NO₃)₂, and (D) NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ brines. The points plotted are apparent boiling points (boiling points not necessarily associated with the eutectic condition).

2.2. Mutual deliquescence and efflorescence relative humidity experiments

We measured the mutual deliquescence (MDRH) and efflorescence (MERH) relative humidity of the KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃ salt assemblages from 120 to 180°C by varying the relative humidity and monitoring the resistivity of the salt systems to confirm the elevated boiling points previously measured for these salt systems (see section 2.1, Rard 2004, 2005). The basic premise behind the resistivity experiments is that the resistance will significantly drop at the MDRH for a given salt mixture as the brine solution forms. Likewise efflorescence will correspond to a significant increase in resistance as the brine solution dries out to form the solid salt mixture. This approach has also been used to measure the DRH of pure salts and NaCl-KNO₃ salt mixtures to 86°C (Yang et al, 2002). It is important to confirm the boiling point measurements with an independent set of experiments, because the current TSPA model initiates localized

corrosion of Alloy 22 for all solutions above 160°C (BSC 2004b). The data we obtained are given in DTN: LL050903412251.150.

2.2.1. Methods

All mutual deliquescence/efflorescence relative humidity experiments were conducted in environmental chambers to control temperature and relative humidity. Temperature was limited to a maximum of 180°C to prevent deterioration of the relative humidity probe. Relative humidity was limited to the maximum achievable value at atmospheric pressure. Pre- and post-calibrations of the relative humidity probes were made using the bi-thermal apparatus described in section 2.3. Uncertainty is calculated as the standard deviation of the pre- and post-calibration RH values.

Resistivity was measured using two parallel platinum electrodes spaced less than one millimeter apart over a recessed reaction cell made of PPS (polyphenylene sulfide; good above 180°C). The length of the electrodes exposed to the solution was about 2.5cm. Comparison of experiments conducted with a quartz slide as inert surface and PPS suggest that PPS is also inert to brine chemistry with no sorption of water at low relative humidity and high temperature (Carroll et al., 2005a). Resistance was monitored by an automated data acquisition system with a Gamry PCI4/300 Potentiostat in which one Pt-electrode was the working electrode and the other was the reference electrode. All measurements were recorded in electrochemical impedance spectroscopy (EIS) mode at 5000 hertz. The voltage reference and the direct current voltage bias were set to zero, with an alternating current voltage of 20 or 25mv. Temperature and relative humidity inside the environmental chamber were measured just above the cells.

All experiments started with enough dissolved salt to provide a conductive path between the electrodes (about 80% coverage of the area between the electrodes). The temperature was then increased to the desired run temperature and the relative humidity was lowered to achieve complete dryout of the salt solution, a condition which was marked by the appearance of high resistivity. The relative humidity was then increased in 2 RH% increments and held for six hours between increments to avoid recording intermediate events. The RH% was increased several units beyond the mutual deliquescence relative humidity, which is marked by a sharp reduction in resistivity. The process is then reversed to measure the mutual efflorescence relative humidity by stepping down in relative humidity. Cells were cleaned and the impedance checked before each new solution was added.

2.2.2. Results and Discussion

Table 2.1 and Figures 2.2 and 2.3 show the mutual deliquescence/efflorescence relative humidity for NaCl-KNO₃-NaNO₃ and KNO₃-NaNO₃ salt mixtures from 120 to 180°C. The drop in impedance clearly shows the absorption of water vapor by the salt assemblage. Figure 2.2 shows a three to four decade drop in impedance for NaCl-KNO₃-NaNO₃ salt mixtures at MDRH of 25.9% at 120°C and 10.8% at 180°C indicating the presence of a brine solution at temperatures much higher than the predicted dryout temperatures of about 140°C at 1 bar (136°C at 0.9 bar, BSC 2004a, Table 6.7-22). As expected, there is a decrease in MDRH with increasing temperature. Deliquescence of

the salt mixture is reversible as is indicated by the general agreement between MDRH and MERH values. Generally, mutual efflorescence relative humidity is about 1 RH% below the mutual deliquescence relative humidity at a specific temperature. This is within the general level of uncertainty in measuring the RH.

Figure 2.3 shows a three to four decade drop in impedance for $\text{KNO}_3\text{-NaNO}_3$ salt mixture at MDRH of 26.4% at 120°C and 20.0% at 150°C. General agreement between MDRH and ERDH values show that deliquescence of the $\text{KNO}_3\text{-NaNO}_3$ is a reversible process. As was the case with the three salt mixture, the MERH is about 1 RH% below MDRH. The $\text{KNO}_3\text{-NaNO}_3$ salt mixture deliquesces at a slightly higher relative humidity (0.5 to 2 RH% units) than the three salt system composed of these salts and NaCl. One explanation for the similar relative humidity values for these two systems is that the $\text{NaCl-KNO}_3\text{-NaNO}_3$ system is dominated by potassium nitrate and sodium nitrate chemistry. This explanation is supported by high nitrate to chloride ratios measured near the eutectic for $\text{NaCl-KNO}_3\text{-NaNO}_3$ (see Section 4.1) and NaCl-KNO_3 mixtures (Carroll et al, 2005c). Addition of NaCl to the nitrate salts appears to stabilize the brine to significantly higher temperatures.

The $\text{KNO}_3\text{-NaNO}_3$ salt mixture should not deliquesce above its boiling point of 160°C (Rard 2004). However our experiments show that $\text{KNO}_3\text{-NaNO}_3$ salt mixtures absorb water at 180°C (Figure 2.3). This observation was also made in preliminary experiments (Carroll et al, 2005a). It is possible that the observed one to two decade drop in impedance at 180°C reflects absorption of monolayers of water rather than full thermodynamic deliquescence observed in boiling point and solubility experiments (Carroll et al., 2005c, Rard 2004). This explanation is consistent with observed absorption of water at relative humidity lower than the equilibrium deliquescence in similar salt mixtures (Ge et al, 1998; Yang et al, 2002). We do not think that one to two decade drop in impedance is an artifact of temperature of the experiment, because a much larger drop was observed at 180°C for the $\text{NaCl-KNO}_3\text{-NaNO}_3$ salt assemblage (Figure 2.2).

Table 2.1. Mutual deliquescence/efflorescence relative humidity (MDRH/MERH) for $\text{NaCl-KNO}_3\text{-NaNO}_3$ and $\text{KNO}_3\text{-NaNO}_3$ salt mixtures from 120 to 180°C. All RH% values have been corrected against steam table standards (Section 2.4).

Temperature °C	%MDRH	%MERH
$\text{NaCl-KNO}_3\text{-NaNO}_3$		
120	25.9±1.0	25.0±1.0
135	21.8±0.9	20.8±0.9
150	18.1±0.9	17.1±0.9
180	10.5±0.8	10.2±0.8
$\text{KNO}_3\text{-NaNO}_3$		
120	26.4±0.4	25.2±0.4
135	23.8±1.0	22.9±1.0
150	20.0±0.9	19.0±0.9
180	10.6±0.2	10.6±0.2

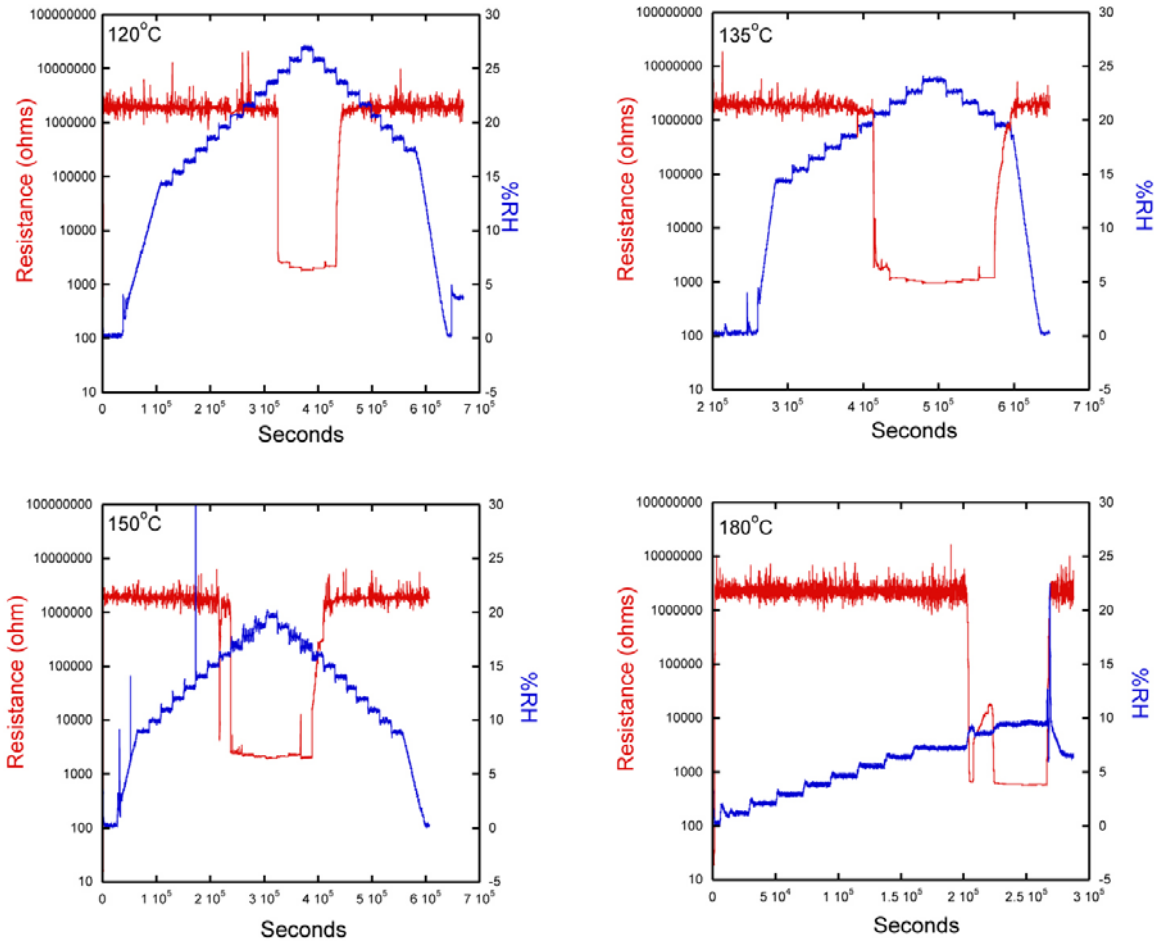


Figure 2.2. Measurement of mutual deliquescence/efflorescence relative humidity for NaCl-KNO₃-NaNO₃ salt mixtures at 120, 135, 150, and 180°C. Mutual deliquescence/efflorescence relative humidity corresponds to drop/increase in resistance as the salt mixtures transform from a solid to solution and back again. RH% values have not been corrected against steam table standards (Section 2.4).

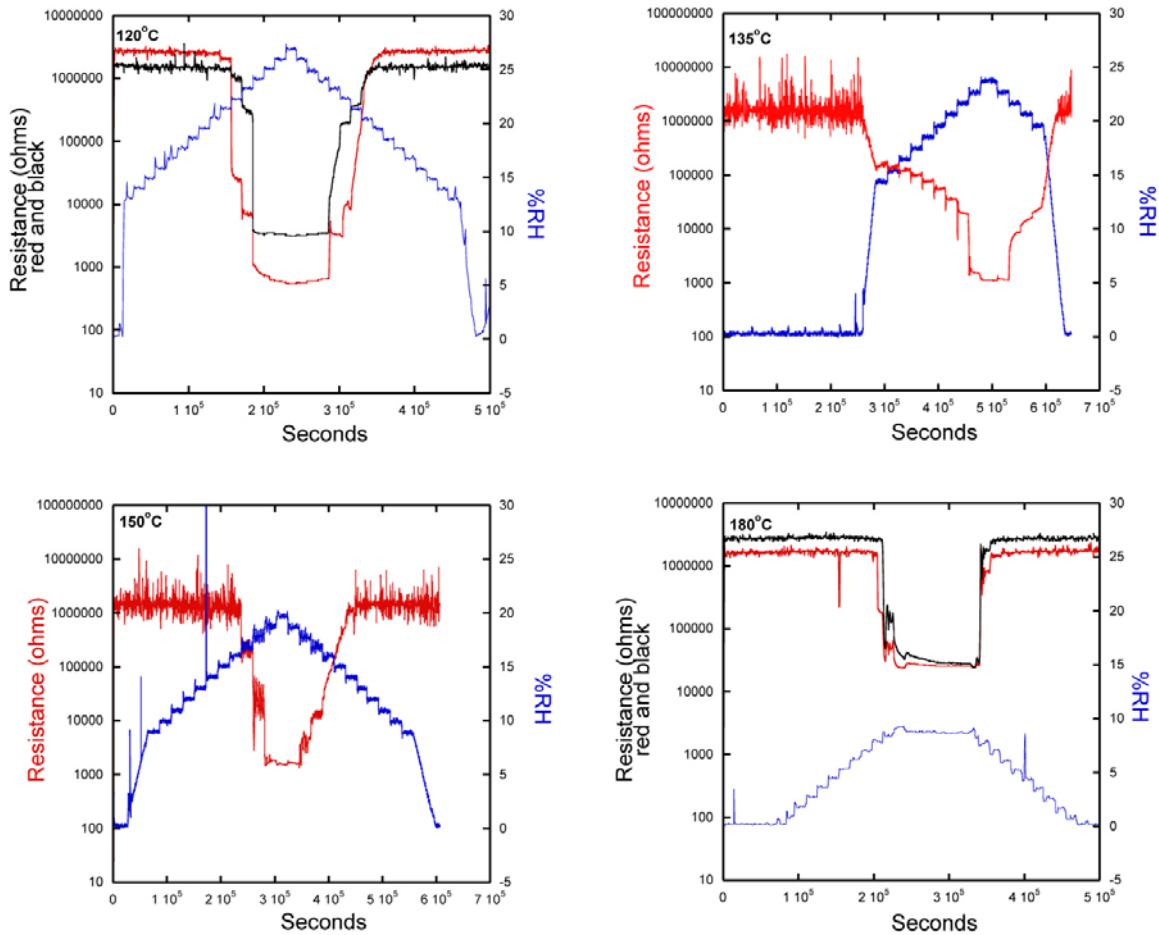


Figure 2.3. Measurement of mutual deliquescence relative humidity for KNO₃-NaNO₃ salt mixtures at 120, 135, 150, and 180°C. Mutual deliquescence/efflorescence relative humidity corresponds to drop/increase in resistance as the salt mixtures transforms from a solid to solution and back again. RH% values have not been corrected against steam table standards (Section 2.4).

2.3. Implications for corrosion at elevated temperatures

Our results show that the brines formed by the deliquescence of salts found in dusts deposited on high level radioactive waste canisters can occur over a much larger temperature and relative humidity window than is represented by Pitzer model calculations (BSC 2004a, Section 6.7.2.13; BSC 2005a). Figure 2.4 compares Pitzer model predictions and experimental measurements of the MDRH for the NaCl-KNO₃, NaCl-KNO₃-NaNO₃, and the KNO₃-NaNO₃ salt mixtures. When brine chemistry is limited by the deliquescence of NaCl-KNO₃ as is predicted from tunnel dust analysis, both model and experiments show that aqueous solutions will form when repository RH > 37% and T < 127°C. When the brine chemistry is limited by the deliquescence of NaCl-KNO₃-NaNO₃, then brines can form at temperatures as high as 220°C and RH as low as 5% as is indicated by the continuous transition of NaCl-KNO₃-NaNO₃ brine to a hydrous molten salt at its melting point (see Section 2.1). The KNO₃-NaNO₃ salt mixture represents the key deliquescent salt assemblage if chloride degasses as HCl(g) at

elevated temperatures. Calculations predict precipitation of a Na-carbonate solid to accompany HCl(g) degassing in addition to the remaining nitrate salts (BSC 2005a). Here we use $\text{KNO}_3\text{-NaNO}_3$ as an analog, because the nitrates are much more soluble than the carbonates and should control the deliquescent behavior. Our experimental results show that if the $\text{NaCl-KNO}_3\text{-NaNO}_3$ loses chloride, then dryout will occur near 160°C , shrinking the brine-window in temperature and relative humidity space. For these three assemblages the existing Pitzer model is able to predict the MDRH for only the NaCl-KNO_3 system. The model under predicts the RH and T range for deliquescence of the $\text{KNO}_3\text{-NaNO}_3$ and $\text{NaCl-KNO}_3\text{-NaNO}_3$ salt mixtures. Boiling point experiments for the $\text{NaCl-KNO}_3\text{-NaNO}_3\text{-Ca(NO}_3)_2$ mixtures show that they form concentrated brines at very high temperatures and consequently very low relative humidity.

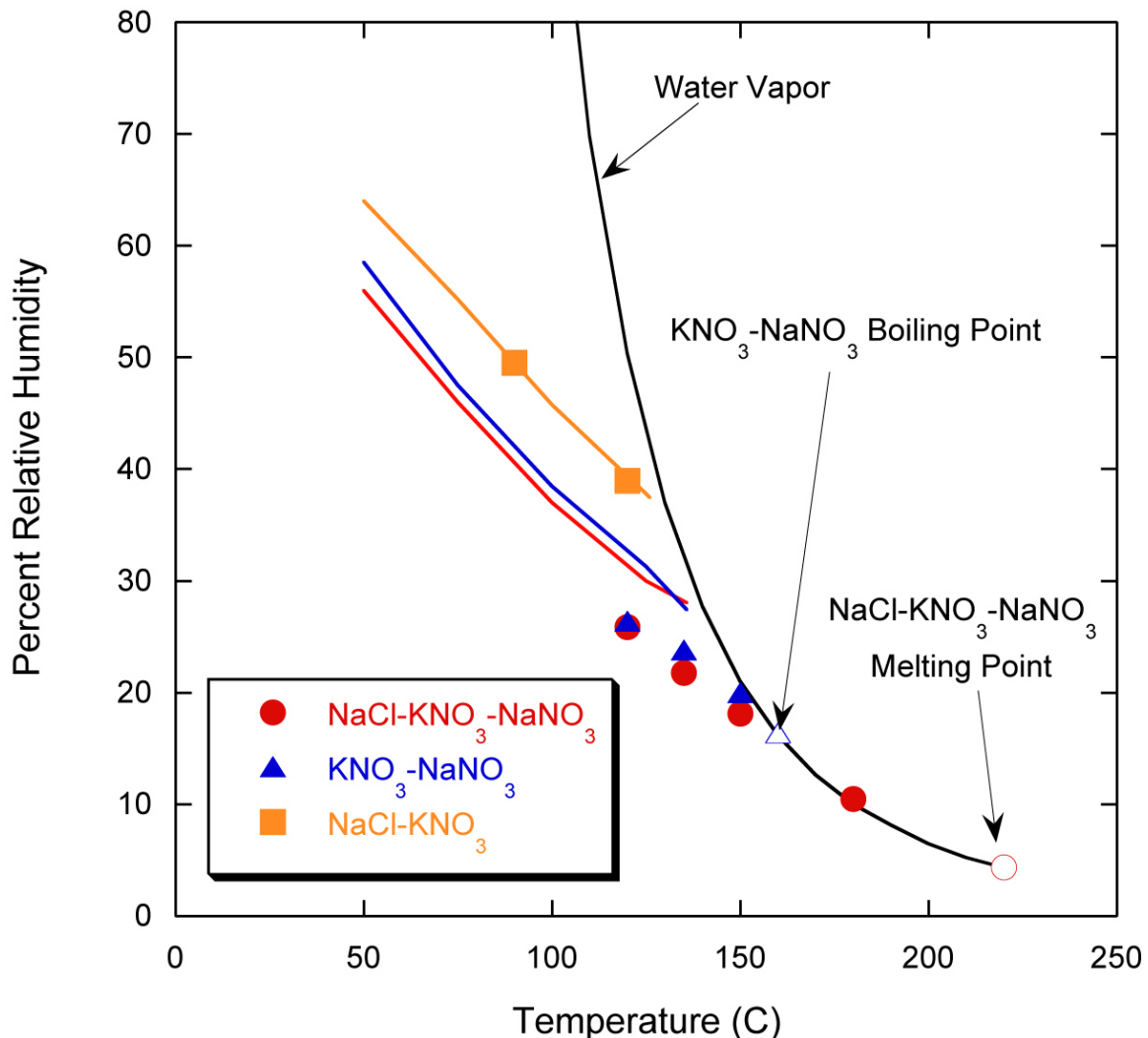


Figure 2.4. Comparison of measured and modeled mutual deliquescence relative humidity for NaCl-KNO_3 (Carroll et al., 2005c) $\text{KNO}_3\text{-NaNO}_3$, and $\text{NaCl-KNO}_3\text{-NaNO}_3$ salt mixtures as a function of temperature. RH% values have been corrected against steam table standards (Section 2.4).

2.4. Bi-thermal Calibration of Relative Humidity Probes

A bi-thermal method was developed to calibrate relative humidity probes at temperatures between 115°C and 180°C. This system was developed because boiling point experiments and geochemical calculations indicated that brines formed by the deliquescence of salt mixtures form at low relative humidity and high temperatures (Carroll et al., 2005a). Current Yucca Mountain Relative humidity probes used in LLNL experiments are calibrated by a Q-vendor (Thunder Scientific) 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. The manufacturer, Vaisala Inc., claims that the relative humidity probes are accurate to $\pm(0.025 \times \text{RH}\%) + 0.5\%$ independent of temperature when calibrated against a high quality certified standard, but they do not provide data to support this claim.

The bi-thermal apparatus for relative humidity calibration at temperatures between 115 and 180°C is a modification of a bi-thermal system developed by Stokes and Robinson (1947) to measure water activity (or relative humidity) in electrolyte solutions. We used the bi-thermal apparatus to calibrate the relative humidity probes by equilibrating water vapor between two vessels at two different temperatures. The lower temperature reservoir contains boiling pure liquid water at 100°C; the higher temperature reservoir contains only a vapor phase (no liquid water or solution is present). After diffusion of water vapor between the two reservoirs for a sufficient period of time the water vapor pressure will be the same in the two reservoirs. However, the water vapor pressure in the higher temperature reservoir $p_{w,T2}$ will be below saturation at that temperature. Pressure equilibrium requires that:

$$p_{w,T2} = p_w^{\circ} T1 \quad (1)$$

The relative humidity in the lower temperature reservoir will always be 100% at the liquid water/water vapor interface. In the higher temperature reservoir the relative humidity is given by:

$$\text{RH}_{T2} = 100(p_{w,T2} / p_w^{\circ} T2) \quad (2)$$

Substitution of equation (1) into (2) yields an expression for the relative humidity of the higher temperature reservoir as a unique ratio of the saturation vapor pressures of pure water at the two temperatures T_2 and T_1 (Table 2.2):

$$\text{RH}_{T2} = 100\{p_w^{\circ}(T1) / p_w^{\circ}(T2)\} \quad (3)$$

We used the temperature dependence of vapor pressure of water from the steam tables in the *CRC Handbook of Chemistry and Physics*, 68th edition (Weast et al., 1987, p. D-189 to D-191) as our standard (Table 2.2, Figure 2.5), because no NIST standard is available for the calibration of relative humidity probes to temperatures above 60°C. Steam tables from the earlier 62nd edition (Weast and Astle, 1981, p. D-168-D-169) containing apparently identical data were qualified as product output (after units conversion of torr to kPa) in the *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier* AMR (BSC 2004a, DTN: LL040601512251.103). We note that steam tables are

also built into the NUFT 3.0 code used to calculate the thermal budget of the repository (BSC 2005b: *Multiscale Thermohydrologic Model*). Determination of percent relative humidity from the steam tables still requires that the temperature probes are calibrated against a NIST traceable standard. The relative humidity probes used in our experiments contain separate temperature sensors that were calibrated against a NIST traceable standard (DP251) in a Omega CL-740A thermal well (Table 2.3). The bi-thermal apparatus allows calibration from 100°C and 100% RH to 180°C and 10% RH.

The bi-thermal apparatus used to calibrate relative humidity at elevated temperatures is shown schematically in Figure 2.6. The setup consists of two connected glass vessels (1 L) in convection ovens to control temperature, one to three RH and T probes for calibration, a NIST traceable temperature probe, a computer based data acquisition system, other temperature sensors, and temperature controllers. A central valve in the connection tube between the two vessels is used to purge the system. The tube is connected to the vessels through a port in the top of the ovens using both glass and Teflon fittings. Heat loss and condensation are prevented by heating the connection tube with regulated heat tape (Digi-Sense temperature controllers and type 'K' OMEGA SA1-K surface mount thermocouples). Oven temperatures are controlled by a computer data acquisition system and RTD (Resistance Temperature Detector) sensors calibrated against the NIST traceable temperature probe (Table 2.3). The data acquisition system measures temperature at several locations in the system to monitor uniform environment.

The relative humidity probes are calibrated from 115 to 180°C, by placing the probes and corresponding temperature probes in higher temperature vessel ports through a soft silicone stopper. All unused ports are sealed with soft silicone stoppers. Prior to beginning the calibration, the system is conditioned by heating vessel T2 and the connection tube above 100°C, and by heating vessel T1 with about 500 ml of pure water to boiling (oven temperature is about 160°C). The warm up period takes between 2 and 4 hours and is monitored by the data acquisition system. Additional water may need to be added to vessel T1 as the system temperature stabilizes. A 5 to 7 point calibration from 115 to 180°C is then conducted by raising the temperature of vessel T2 to a given value, allowing the temperature to stabilize, and measuring relative humidity and temperature in triplicate using the RH probe sensors. The temperature in vessel T2 is changed and the process is repeated.

Figure 2.7 shows the calibration results used for probes Z1420005, Z1420006, and T4610030 made from December 2004 to August 2005. The response of the measured RH compared to the standard RH calculated from steam tables and Q temperature measurements are linear with small drift between the pre and post experiment calibrations. Percent RH was calibrated against a linear regression of the combined pre- and post-calibration runs. Uncertainty in RH is calculated as the standard deviation of RH calculated for the pre- and post-calibration runs separately and is typically less than 1.5 RH% units.

Table 2.2. Relative humidity standard based on vapor pressure of water from 100 to 180°C.

Temperature (°C)	Vapor Pressure (mm), (Weast et al. 1987).	Relative Humidity (%)
100	760.00	100.00
105	906.07	83.88
110	1074.56	70.72
115	1267.98	59.94
120	1489.14	51.04
125	1740.93	43.65
130	2026.16	37.51
135	2347.26	32.38
140	2710.92	28.03
145	3116.76	24.38
150	3570.48	21.29
155	4075.88	18.65
160	4636.00	16.39
165	5256.16	14.46
170	5940.92	12.79
175	6694.08	11.35
180	7520.20	10.11
185	8423.84	9.02
190	9413.36	8.07
195	10488.76	7.25
200	11659.16	6.52
205	1292.12	5.88

Table 2.3. Comparison of calibrated RTD temperature sensors against NIST traceable standard, DP251.

NIST traceable Temperature Probe °C		RTD °C		RH Probe °C		
DP251 Channel A	DP251 Channel B	Oven T1 GG510	Oven T2 GG511	T4610030	Z1420005	Z1430006
20.0	20.1	20.1	20.1			
	50.0			49.9	49.9	49.9
75.1	75.0	74.9	74.9			
	99.7			99.5	99.5	99.6
	124.4			124.2	124.2	124.2
140.2	140.1	140.0	140.0			
	149.3			149.1	149.2	149.2
	179.4			179.2	179.3	179.4

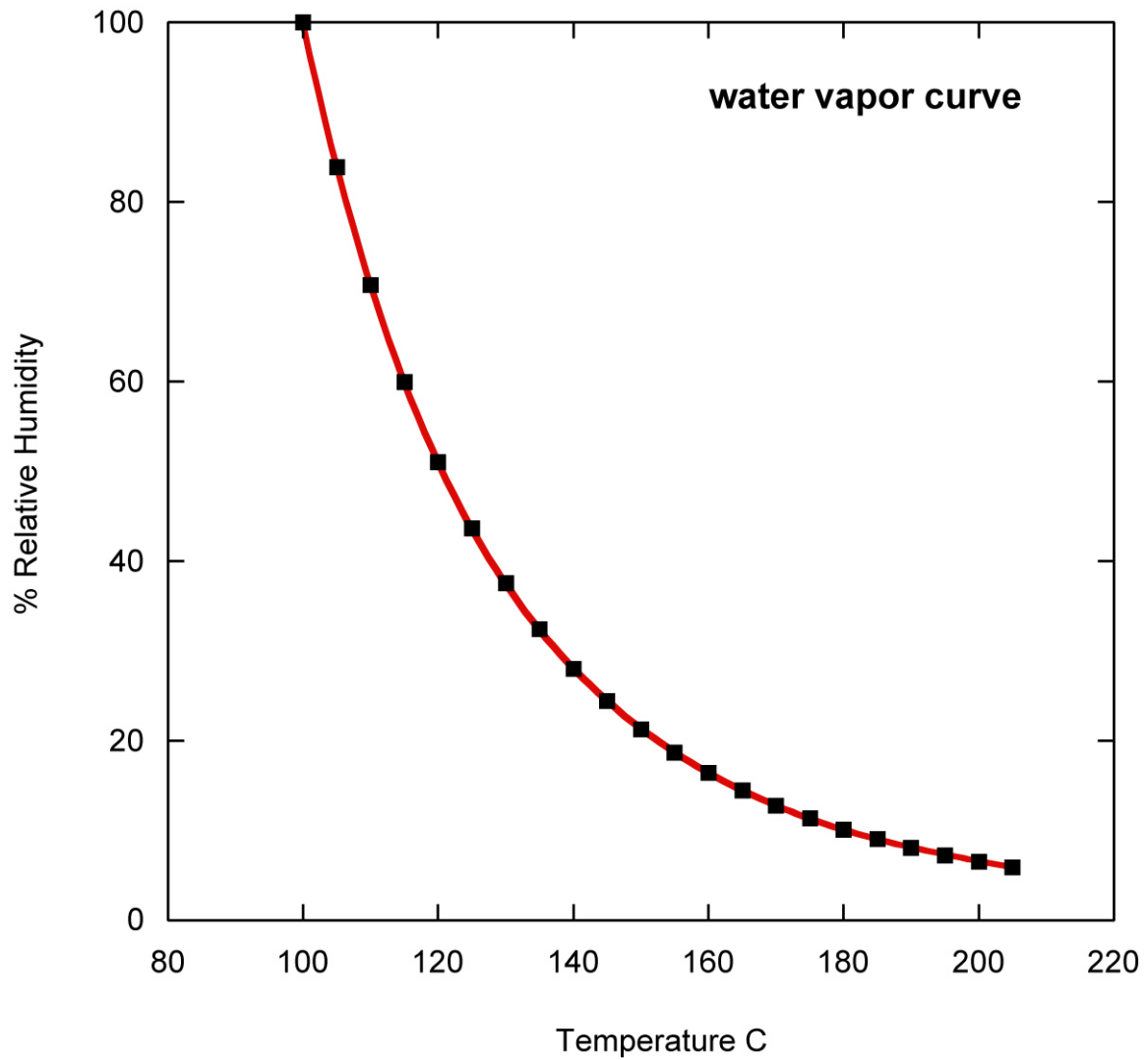


Figure 2.5. Temperature dependence of the vapor pressure of pure water. (Weast et al. 1987).

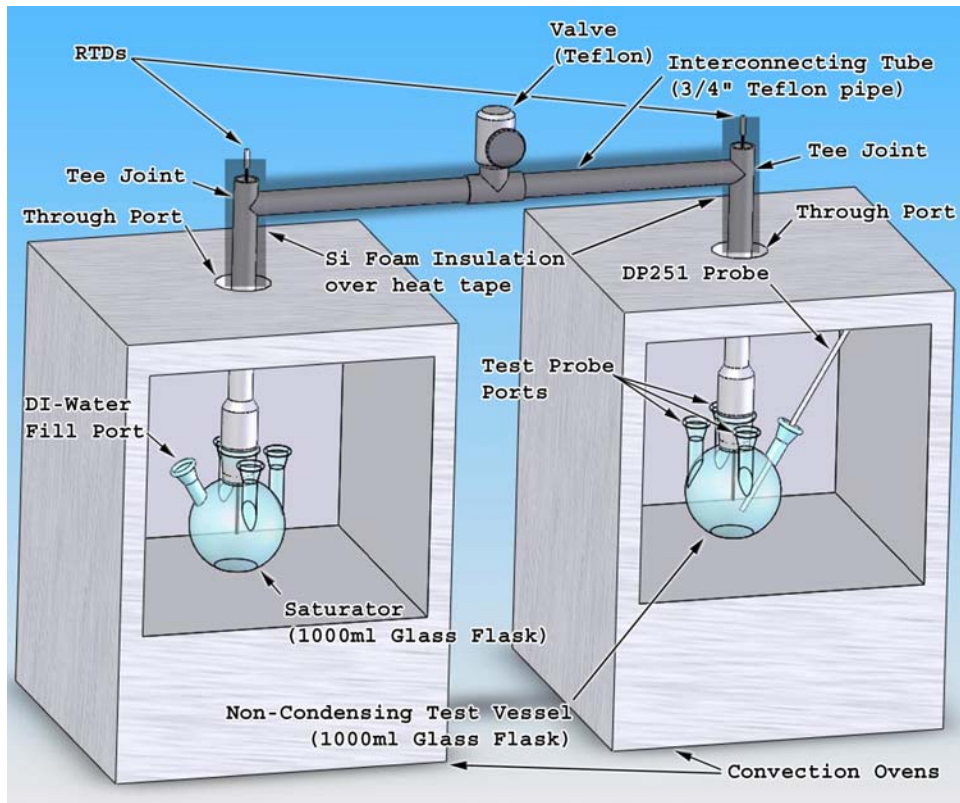


Figure 2.6. Schematic of the bi-thermal apparatus used for calibration of RH at elevated temperature.

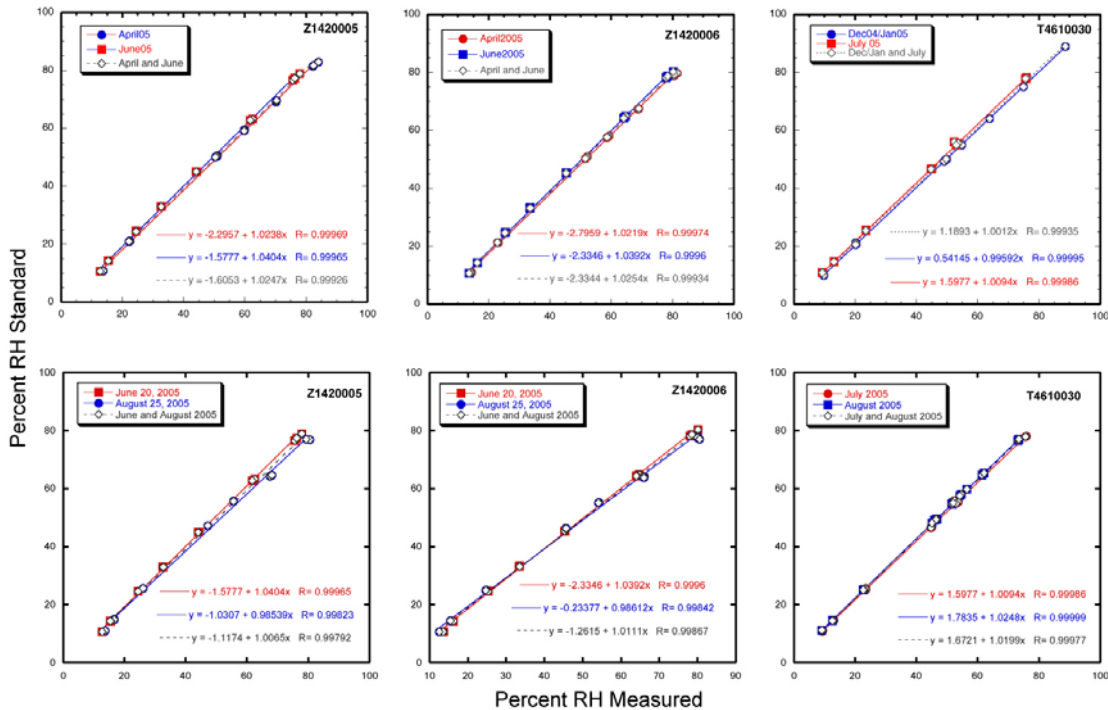


Figure 2.7. Relative humidity calibration. Percent RH Standard was calculated using data for the vapor pressure of water over pure liquid water (Table 1). The temperature was determined using a Q temperature sensor within the RH probe.

3. If brines form at elevated temperature will they persist?

3.1. Stability of NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ Brines

Section 2 clearly demonstrates that NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ brines form at elevated temperature and low relative humidity, suggesting water will be present over the lifetime of the repository. Thermodynamically it is possible for these brines to lose HCl(g) and HNO₃(g) to form solutions that are stable over a narrower relative humidity and temperature range as is argued in the *Analysis of Dust Deliquescence for FEP Screening* (BSC, 2005a) and shown experimentally (the present report, Section 2.3, Figure 2.4). Although CaCl₂ and MgCl₂ brines readily degas (Carroll et al, 2005a), NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ brines do not. Thermogravimetric analysis and subsequent solution analysis of the residual salts have shown no evidence of loss of Cl or NO₃ relative to the balancing cations (DTN: LL050205123121.047). It is possible that this is an artifact of the experimental method. If small amounts of HCl(g) and HNO₃(g) degassed, they were not be detected in the wet chemical analysis of the residual solids.

3.2. Stability of Ammonium Salts

Ammonium salts (sulfates, nitrate, and chlorides) are common components in atmospheric dust, which may be entrained in the repository during the ventilation stage of the repository. Current understanding of brine formation from deliquescent salts was based on water leachates from tunnel dusts that did not analyze for ammonium (BSC 2004a). However, re-analysis of these tunnel dust leachates shows that ammonium is present (DTN GS050408313000.001). In this section we address the stability of ammonium salts in a repository environment (source DTN: LL050301723121.050, LL050205223121.048, and LL050600123121.052).

Ammonium nitrate and ammonium chloride salts are highly volatile and decompose over very short time periods. The experimental results described below suggest that all ammonium, nitrate, and chloride tied to these salts can be removed from bulk water analyses of dust leachates that are used to estimate key salt assemblages for brine formation after the ventilation period because these salts will have decomposed to their gas components. Ammonium nitrate decomposition is strongly dependent on temperature with an activation energy, $E_a = 92 \text{ kJ mol}^{-1}$ calculated from experiments conducted between 147 and 190°C (Vyazovkin et al., 2001). Thus ammonium nitrate solids will completely decompose to gas products, presumably $\text{NH}_3(\text{g})$ and $\text{HNO}_3(\text{g})$, within 40 minutes at 200°C and 9 hours at 150°C. Ammonium chloride exhibits similar decomposition behavior as ammonium nitrate, with a measured $E_a = 89 \text{ kJ mol}^{-1}$ calculated from thermo gravimetric experiments from 100 to 250°C (Figure 3.1). Thus ammonium chloride will completely decompose, presumably to $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$, in about 2 minutes at 250°C and about 4 days at 100°C.

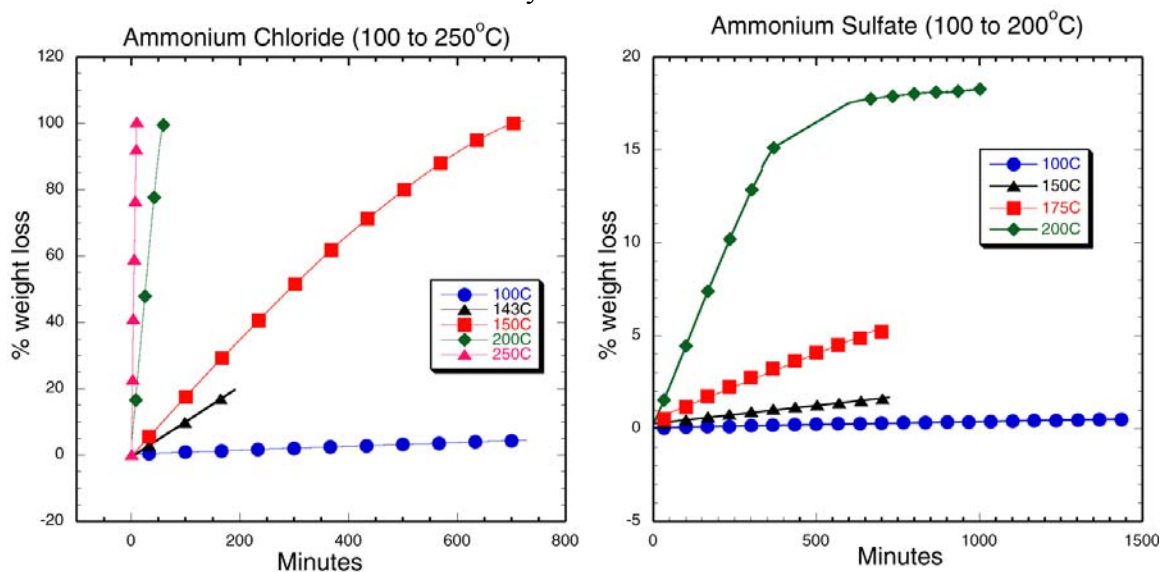


Figure 3.1. Decomposition of dry ammonium chloride (100 to 250°C) and ammonium sulfate (100 to 200°C) salts determined by weight loss using a thermogravimetric analyzer.

In contrast to ammonium nitrate and ammonium chloride salts, ammonium sulfate is more kinetically stable and has a more complex degassing behavior that may reflect changes in surface area or solid phase chemistry (Figure 3.1). In general, the rate of decomposition increases with increasing temperature from 100 to 250°C; however, there

is a second-stage, slower weight-loss period that was observed only in the 200°C and 250°C experiments. Here the rate is about 20 times slower than in the first-stage period. It is possible that the first-stage rate corresponds to the transformation of ammonium sulfate to ammonium bisulfate (NH_4HSO_4), while the second, slower rate reflects the decomposition of the bisulfate. Simple linear extrapolation of the 100°C rate data shown in Figure 3.1 suggests that ammonium sulfate will completely decompose to its gas components within a year at this temperature (0.5% sublimation after 1 day at 100°C implies complete sublimation after 200 days). However, this may greatly overestimate the loss of $\text{NH}_3(\text{g})$ and $\text{H}_2\text{SO}_4(\text{g})$ from salts present in dust, because it is not known if the decomposition of ammonium sulfate at this temperature will eventually be limited by a second-stage, slower rate.

Ammonium nitrate, ammonium chloride, and possibly ammonium sulfate will decompose rapidly, releasing ammonia and a mineral acid (HCl , HNO_3 , or H_2SO_4), with the net effect of removing ammonium salts from the dust system prior to deliquescence. The tunnel dust deliquescence modeling carried out to date did not include ammonium, but neither did it account for the anionic component (Cl^- , NO_3^- , or SO_4^{2-}) that would be removed along with the ammonium.

4. If brines persist will they be corrosive?

Brines formed by the deliquescence of $\text{NaCl-KNO}_3\text{-NaNO}_3$ salt mixtures at 120°C are dominated by high nitrate concentrations and have $\text{NO}_3:\text{Cl} = 10:1$ near the eutectic composition. Nitrate concentrations and $\text{NO}_3:\text{Cl}$ increase with increasing temperature in the NaCl-KNO_3 system (Carroll et al 2005c). We expect this to be the case also for the $\text{NaCl-KNO}_3\text{-NaNO}_3$ system as it approaches its maximum apparent boiling point (before it grades into a hydrous melt stable to at least that temperature). High nitrate and $\text{NO}_3:\text{Cl}$ suggest that localized corrosion will be minimal in the brines formed by dust deliquescence, because electrochemical tests show that nitrate inhibits corrosion when the $\text{NO}_3:\text{Cl} > 0.5:1$ (Felker et al. 2005). However localized corrosion has been observed in recent long-term corrosion studies in Na-K-Cl-NO_3 brines with $\text{NO}_3:\text{Cl} = 0.5$ and 7.4 at 160 and 220°C (Dixit et al, 2005).

In this section we discuss the solubility of $\text{NaCl-KNO}_3\text{-NaNO}_3$ salt mixture at 120°C and briefly discuss the results of the long-term, high temperature corrosion experiments (details may be found in Dixit et al., 2005)

4.1. Solubility of $\text{NaCl-KNO}_3\text{-NaNO}_3$ salt mixture at 120°C

4.1.1. Methods

We measured brine composition at controlled relative humidity for the $\text{NaCl-KNO}_3\text{-NaNO}_3$ salt mixture at 120°C as a function of aqueous X_{NO_3} . We approached the equilibrium brine composition by placing identical mole fractions of dissolved and solid salt mixtures in an environmental chamber at controlled relative humidity and temperature. Under these conditions the dissolved salt mixture (labeled A) evaporates concentrating the solution and precipitating one to four salts (NaCl , KCl , NaNO_3 and/or KNO_3), and the solid salt mixture (labeled B) absorbs water dissolving the salts until equilibrium is reached. Calibrated temperature and relative humidity probes were placed

just above the salts in beaker B. Relative humidity probe calibrations were made using the bi-thermal apparatus described in section 2.4. The probes used in this study were Z1420005 and Z1420006 (Figure 2.7).

Brines were sampled in-situ at experimental temperature and humidity. To do this, a PFA Teflon tube was placed just above the bottom of both the A and B beakers. The tube was connected to a 250ml vacuum filter flask containing a 1.0 μ m filter. Between 2 to 20 grams of sample were pulled through the vacuum flask and 1.0 μ m filter via the external vacuum pump. The samples were diluted in the flasks with 18M Ω water to a total solution weight of about 200g. The diluted samples were transferred to plastic bottles for analysis. All dilution factors were determined gravimetrically. Solution composition was determined using ion chromatography.

4.1.2. Results and Discussion

Solubility of NaCl-KNO₃-NaNO₃ salt mixtures at 120°C is plotted in Figure 4.1 as percent relative humidity and solution composition versus mole fraction of nitrate in the dissolved phase. In contrast to past results reported for the NaCl-KNO₃ system (Carroll et al., 2005c), the solution composition and RH% approached, but did not achieve equilibrium. Figure 4.1 suggests that the eutectic relative humidity occurs at RH near 40% and $X_{\text{NO}_3} = 0.95$. This value is higher than the 25.9 %RH determined in the resistivity experiments for the same salt mixture at 120°C (Table 2.1). Additionally, the solution compositions measured from the initially dissolved and initially solid salt mixtures do not converge as they should if the brines were at equilibrium. Compositions at $X_{\text{NO}_3} > 0.9$ differ by as much as 16 molal for dissolved nitrate. Solution compositions below $X_{\text{NO}_3} = 0.9$ do converge and represent equilibrium compositions and RH. Trends in the RH data below $X_{\text{NO}_3} = 0.9$ suggest that the MDRH brine is a high nitrate brine with NO₃:Cl ratios between 10 and 99 (corresponding to $X_{\text{NO}_3} = 0.90$ and 0.99), where the nitrate could exceed 90 molal.

Our results show that brines formed from the deliquescence Na-K-Cl-NO₃ salts are dominated by nitrate and exceed the nominal NO₃:Cl = 0.5 determined to mitigate localized corrosion in Alloy 22 and K-Na-Cl-NO₃ brines from 110 to 140°C determined from 24 hour cyclic polarization experiments with NO₃:Cl between 0.5 and 72 (Felker et al., 2005). In contrast to the short-term electrochemical corrosion studies, passive corrosion studies of Alloy 22 at 160 and 220°C show crevice corrosion after 9 months of reaction in Na-K-Cl-NO₃ brines with NO₃:Cl between 0.5 and 7.4 (Dixit et al., 2005). The discrepancy between the short-term electrochemical and long-term passive corrosion experiments may be attributed to duration, temperature, and/or nitrate concentrations of the experiments. It is worth noting that absolute chloride concentrations in the high temperature long-term experiments are similar to those in the chloride solutions used in the short-term electrochemical experiments, despite having very different NO₃:Cl ratios.

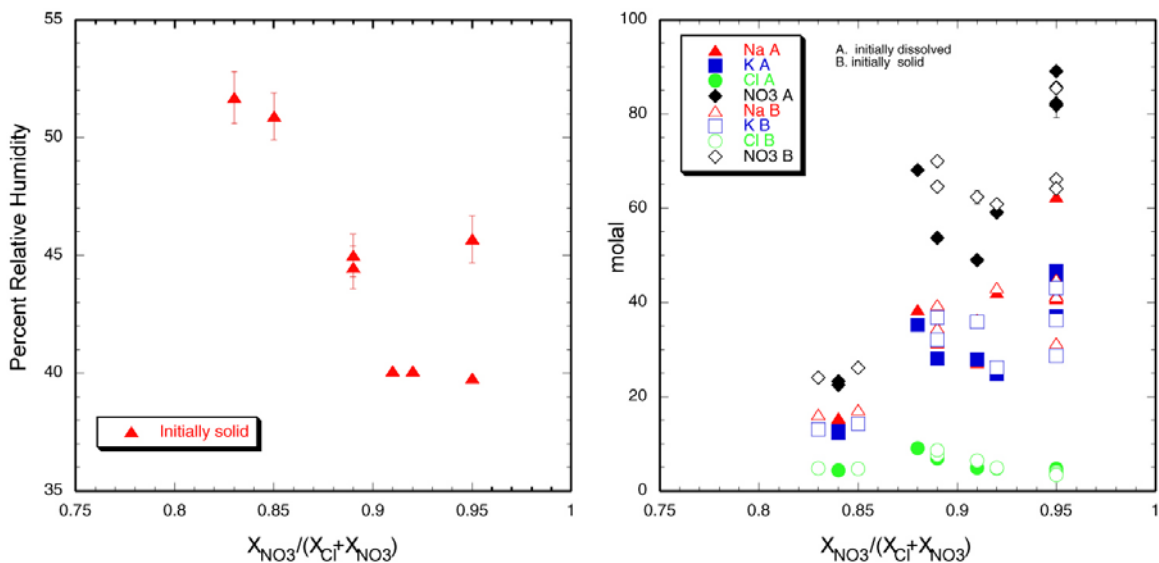


Figure 4.1. Deliquescence of NaCl-KNO₃-NaNO₃ salts at 120°C starting from initially dissolved and initially solid mixtures plotted as (A) per cent relative humidity and (B) solution composition. RH% values have been corrected against steam table standards (Section 2.4).

5. Conclusions

The FY05 Waste Package Environment testing program at Lawrence Livermore National Laboratory focused on determining the temperature, relative humidity, and solution compositions of brines formed due to the deliquescence of NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ salt mixtures. NaCl-KNO₃-NaNO₃ and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ salt mixtures form brines that transform to hydrous melts that do not truly “dry out” due to boiling until temperatures above 300 and 400°C, respectively. As is the case in similar but simpler nitrate-containing systems (e.g., KNO₃, NaNO₃, NaCl-KNO₃), the NaCl-KNO₃-NaNO₃ salt mixture forms brines at lower RH at higher temperature. Its behavior is however relatively extreme. The MDRH for NaCl-KNO₃-NaNO₃ salt mixtures decreases from 25.9% at 120°C to only 10.8% at 180°C. Similarly, the MDRH for the KNO₃-NaNO₃ salt mixture decreases from 26.4% at 120°C to 20.0% at 150°C. Additionally, our experiments show that the KNO₃-NaNO₃ salt mixture absorbs some water (while not fully deliquescing) at 180°C, well above its thermodynamic dryout temperature. Experiments to date are inconclusive regarding the potential for Na-K-Cl-NO₃ brines to degas and lose the corrosive chloride component. However, solid ammonium salts (especially chloride and nitrate) decompose in minutes to days at elevated temperatures. K-Na-NO₃-Cl brines that form at high temperature and low relative humidity are dominated by nitrate chemistry. Nitrate concentrations approach 80 molal and have NO₃:Cl near 10:1 near the eutectic composition of NaCl-KNO₃-NaNO₃ at 120°C. The role of nitrate at elevated temperatures on localized corrosion is an area of active research.

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