



# Experimental Determination and Thermodynamic Calculation of the Deliquescence Relative Humidity of Multicomponent Salt Mixtures

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## INTRODUCTION

Deposition of aerosol and dust from ventilation air and evaporation of groundwater seeping into the drifts of a potential geologic repository for nuclear waste at Yucca Mountain, Nevada may lead to the accumulation of multicomponent salts on the surfaces of engineered barrier components, such as drip shields, waste packages, and ground support materials. These hygroscopic salts will deliquesce, i.e., absorb moisture from humid air, if the relative humidity in the environment reaches the deliquescence relative humidity (DRH) of the salt or salt mixture. Salt deliquescence would generate small volumes of brines that are potentially corrosive to the metallic materials. The DRH of multicomponent salt mixtures depends on temperature and composition, but experimental data are sparse, particularly at temperatures (>80 °C) relevant to a geologic repository for nuclear waste.

In this study, the DRH of salts and salt mixtures in the quaternary system  $\text{Na}^+/\text{K}^+/\text{Cl}^-/\text{NO}_3^-$  was measured at selected temperatures using conductivity cells placed in a temperature and relative humidity controlled chamber. The DRH at other compositions and temperatures was evaluated using the Environmental Simulation Program (ESP) Version 7.0, a chemical process simulator developed by OLI Systems, Inc. for aqueous based systems in industrial and environmental applications. ESP 7.0 incorporates a new thermodynamic model (Wang et al., 2002) and database that can be applied to a concentration range from a pure solvent to a pure solute (e.g., fused salt).

The results of the study will be used to evaluate the chemistry of water contacting the drip shields, waste packages, and ground support materials in the potential Yucca Mountain repository and the time and temperature during which corrosion of the metallic materials could initiate.

## EXPERIMENTAL METHOD

- Conductivity cell (Figure 1)
  - Filter paper (0.23 mm thick  $\times$  26 mm wide  $\times$  46 mm long) [0.0091  $\times$  1.0  $\times$  1.1 in] was wetted with a solution saturated with the salt mixture of interest; the paper helped form an evenly distributed layer of salt deposit between two platinum electrodes
  - The filter paper was placed on an arched supporting surface made of polytetrafluoroethylene (PTFE); the arched surface allowed excess liquid to drain off and kept the thickness of the conducting layer relatively constant
- Conductivity cell was placed inside a high precision humidity chamber (Thunder Scientific Model 2500; Figure 2)
  - Relative humidity (RH) range: 10 to 98 % ( $\pm 0.5$  %)
  - Temperature range: 0 to 70 °C ( $\pm 0.02$  °C) [32 to 158 °F ( $\pm 0.02$  °F)]
- Impedance was measured with a QuadTech Model 7600 Precision LCR Meter
- A frequency of 1,000 Hz was selected for impedance measurements
  - Figure 3 shows typical responses of the impedance between two platinum electrodes to changes in relative humidity and to different frequencies (1,000, 16,000, and 100,000 Hz)
  - Impedances measured at high frequencies were slightly lower than those measured at lower frequencies
  - At low RH, the responses measured at frequencies higher than 1,000 Hz were poor and no response at all was observed at 100,000 Hz
- Impedance was measured going from low to high RH—avoids kinetic barrier to nucleation (efflorescence) when going from high to low RH

## EXPERIMENTAL RESULTS

### Conductivity Measurements

- Figure 4 shows the typical relationship between measured impedance and relative humidity
  - With increasing RH, impedance starts to decrease at an RH ~20 % less than the DRH of the salt mixture, decreases sharply in the vicinity of the DRH, and levels off at even greater RH
  - Mid point of sharp change in impedance in the range  $10^2$  to  $10^5$  ohm was taken as a measure of the DRH
- Figure 5 shows the DRH of salts and salt mixtures derived from conductivity measurements at various temperatures.

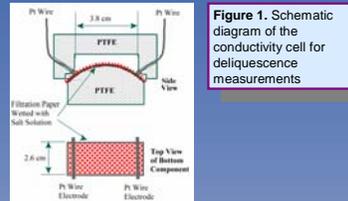


Figure 1. Schematic diagram of the conductivity cell for deliquescence measurements

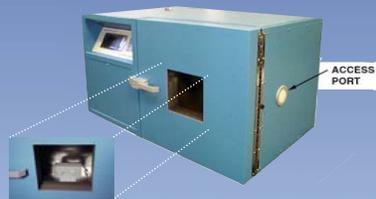


Figure 2. Conductivity cell inside a controlled temperature humidity chamber (Thunder Scientific Model 2500).

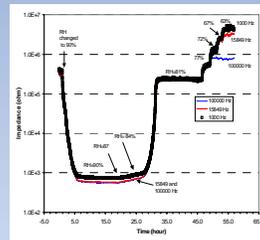


Figure 3. Typical responses of impedance, measured at three frequencies, to changes in relative humidity. The conductivity measurements were done on a saturated KCl solution at 30 °C [86 °F].

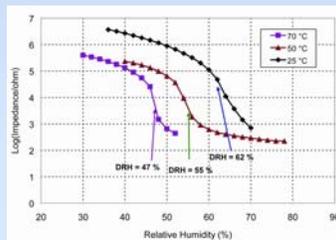


Figure 4. Experimental data for mixtures in the system  $\text{NaCl}+\text{NaNO}_3+\text{KNO}_3$  at 25, 50, and 70 °C [77, 122, and 158 °F] showing the typical relationship between impedance and relative humidity.

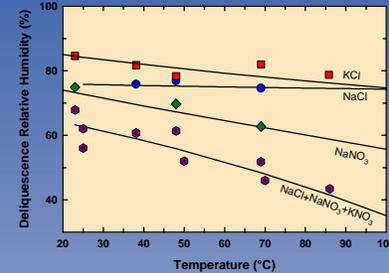


Figure 5. Measured deliquescence relative humidity (DRH, indicated by symbols) as a function of temperature of the single salts KCl, NaCl, and  $\text{NaNO}_3$ , and of the three-salt mixture  $\text{NaCl}+\text{NaNO}_3+\text{KNO}_3$ . The curves indicate the DRH values calculated with Environmental Simulation Program Version 7.0.

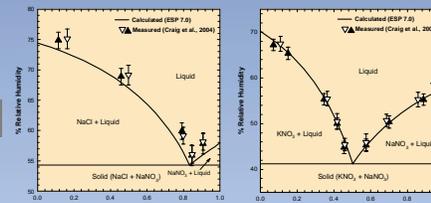


Figure 6. Comparison of published data on deliquescence relative humidity of (a)  $\text{NaCl}-\text{NaNO}_3$  and (b)  $\text{KNO}_3-\text{NaNO}_3$  mixtures at 90 °C [194 °F] (Craig et al., 2004) with values calculated using Environmental Simulation Program Version 7.0.

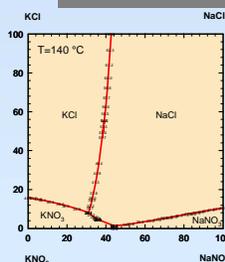
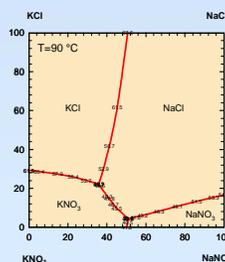
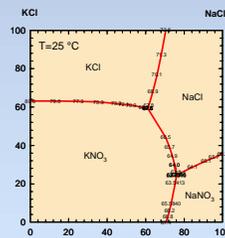


Figure 7. Solubility (mole %) of aqueous solutions saturated with two- or three-salt mixtures in the quaternary system  $\text{Na}^+/\text{K}^+/\text{Cl}^-/\text{NO}_3^-$  at 25, 90, and 140 °C [77, 194, and 284 °F] calculated using the Environmental Simulation Program 7.0. The numbers superimposed on the curves are the calculated DRH (% RH) at selected compositions.

## THERMODYNAMIC MODELING

### Deliquescence Relative Humidity

- The deliquescence relative humidity, DRH, of a salt or salt mixture is given by
 
$$\text{DRH} = \frac{p_{\text{H}_2\text{O}_{\text{sat}}}}{p_{\text{H}_2\text{O}}^0}$$
 where  $p_{\text{H}_2\text{O}_{\text{sat}}}$  is the vapor pressure of an aqueous solution saturated with the salt or salt mixture of interest, and  $p_{\text{H}_2\text{O}}^0$  is the vapor pressure of pure water
- Values of  $p_{\text{H}_2\text{O}_{\text{sat}}}$  and  $p_{\text{H}_2\text{O}}^0$  were calculated using the Environmental Simulation Program Version 7.0

### Environmental Simulation Program Version 7.0

- A steady state chemical process simulator developed by OLI Systems, Inc. (Morris Plains, New Jersey, USA)
- Calculates physical and chemical properties of multiphase, multicomponent aqueous based systems for temperatures to 300 °C [572 °F] and pressures to 1,500 bar [1,400 atm].
- Version 7.0 has a new thermodynamic model (Wang et al., 2002) and database for mixed solvent electrolyte systems applicable to a concentration range from a pure solvent to a pure solute (e.g., fused salt).

### Modeling Results

- Calculated DRHs as a function of temperature of the single salts KCl, NaCl, and  $\text{NaNO}_3$ , and of the salt mixture  $\text{NaCl}+\text{NaNO}_3+\text{KNO}_3$ , are compared with experimental data in Figure 5.
- Calculated DRHs of the  $\text{NaCl}-\text{NaNO}_3$  and  $\text{KNO}_3-\text{NaNO}_3$  systems at 90 °C [194 °F] are compared with experimental data from published literature (Craig et al., 2004) in Figure 6.
- The predicted values of solubility and DRHs in the quaternary system  $\text{Na}^+/\text{K}^+/\text{Cl}^-/\text{NO}_3^-$  at 25, 90, and 140 °C [77, 194, and 284 °F] are shown in Figure 7.

### Summary

- Deliquescence relative humidities of salts and salt mixtures in the system  $\text{Na}^+/\text{K}^+/\text{Cl}^-/\text{NO}_3^-$  calculated using the Environmental Simulation Program 7.0 show good agreement with values measured using a conductivity method.
- Additional experiments are underway at higher temperatures and with salt mixtures containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .
- This work is being conducted as part of ongoing assessments of the significance to waste isolation of near field processes in the potential high level nuclear waste repository at Yucca Mountain, Nevada.

### REFERENCES

- [1] Craig, L., et al. (2004) In *Water Rock Interaction*, R. Wandy and R. Seal, II (eds.), Leiden, The Netherlands, A.A. Balkema, pp. 1275-1278; [2] Wang P., et al. (2002) *Fluid Phase Equilibria* 203, 141-176.

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