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November 21, 2001
Contract No. NRC–02–97–009
Account No. 20–01402–561

U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
Office of Nuclear Material Safety and Safeguards
Program Management, Policy Development, and Staff
Office of the Director
Mail Stop 8D–37
Washington, DC 20555

Subject: Programmatic Review of Papers

Dear Mrs. DeMarco:

The enclosed papers are being submitted for programmatic review. These papers will be submitted for presentation at the Materials Research Society Annual meeting, to be held November 26–29, 2001, in Boston, Massachusetts. The title of these papers are:

"Deliquescence Behavior of Multicomponent Salts: Effects on the Drip Shield and Waste Package Chemical Environment of the Proposed Nuclear Waste Repository at Yucca Mountain, Nevada"
Roberto T. Pabalan, Lietai Yang, and Lauren Browning

"Experimental Determination of the Deliquescence Relative Humidity and Conductivity of Multicomponent Salt Mixtures"
Lietai Yang, Roberto T. Pabalan, and Lauren Browning

These papers are a product of the CNWRA and do not necessarily reflect the view(s) or regulatory position of the NRC.

Please advise me of the results of your programmatic review. Your cooperation in this matter is appreciated.

Sincerely,

Budhi Sagar
Technical Director

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Washington Office • Twinbrook Metro Plaza #210
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

Experimental Determination of the Deliquescence Relative Humidity and Conductivity of Multicomponent Salt Mixtures

Lietai Yang, Roberto T. Pabalan and Lauren Browning
Center for Nuclear Waste Regulatory Analyses,
San Antonio, TX 78238–5166, U.S.A.

ABSTRACT

The conductivity of hygroscopic salt deposits containing Na^+, K^+, NO_3^- and Cl^- ions was measured in air as a function of relative humidity at constant temperatures. The DRHs of multicomponent salts containing Na^+, K^+, NO_3^- and Cl^- were also determined experimentally. The results of the conductivity experiments show that the conductivity of initially dry salt deposits start to increase after reaching a relative humidity value that is 15 to 20% lower than the deliquescence relative humidity (DRH) of the salt. When the DRH is reached, the conductivity increases dramatically as the salt dissolves and transforms into a saturated aqueous phase. The increase in conductivity at humidities below the DRH is attributed to the adsorption of water on the surface of the salt particles. Because of the increase in conductivity, the initiation of aqueous corrosion of metals in contact with hygroscopic salts may occur at a relative humidity much lower than the DRH of the salt. Thus, the onset of aqueous corrosion of metallic nuclear waste package and the drip shield may be earlier, the duration may be longer, and the temperature at which it occurs may be higher than assumed based on the DRH of the salt. The results of the DRH experiments show that the DRH of a salt mixture is usually significantly lower than that of any of its component pure salt.

INTRODUCTION

Deposition of aerosol and dust from ventilation air and the evaporation of water seeping into the drift of a proposed geologic repository at Yucca Mountain, Nevada, may lead to the accumulation of hygroscopic salts on drip shield and waste package surfaces [1–3]. These hygroscopic salts will sorb moisture from the atmosphere and form brine solutions, potentially causing aqueous corrosion of the drip shield and waste package. The U.S. Department of Energy (DOE) performance assessment model assumes that aqueous corrosion of waste package and drip shield begins when the relative humidity reaches the DRH of pure $NaNO_3$ salt in the temperature range that was predicted for the geological repository system [1,4]. Aqueous corrosion requires the presence of an electrolyte that is conductive to ionic species. In this study, the relative values of ionic conductivity of various salts were measured as a function of relative humidity at constant temperatures. The minimum relative humidity at which conductivity starts to rise was compared to the DRH of the salt. Also, because DRH data for salt mixtures containing Na^+, K^+, NO_3^- and Cl^- are not available from the literature, these were experimentally determined at the same temperatures as the conductivity tests.

EXPERIMENTAL

The DRH of salt mixtures was measured using a hygrometer (Model 4085CC, Control Company, TX, USA) with a ±1.5% accuracy. The test set-up is shown in Figure 1. The

measurement was conducted according to the procedures given by the American Society for Testing and Materials standard (ASTM E104) [5]. Both the glass flask and the hygrometer were placed in an oven (Model 838F, Fisher Scientific). The temperature was held constant for at least 30 min before each measurement was made. The temperature reading of the built-in temperature sensor of the hygrometer was recorded as the saturation temperature. During the experiment, identical glass flasks containing pure salt solutions of NaCl, $NaNO_3$, KNO_3, KCl and $MgCl_2$ were also placed in the oven and used as controls for verifying and correcting the hygrometer readings based on their DRH values published in the literature [6]. A comparison between the measured and published DRH for these salts in the temperature range of 23 to 86 °C is presented in Table 1. The 99% confidence interval for the agreement in the relative humidity range of 25 to 86% is ±1.51%.

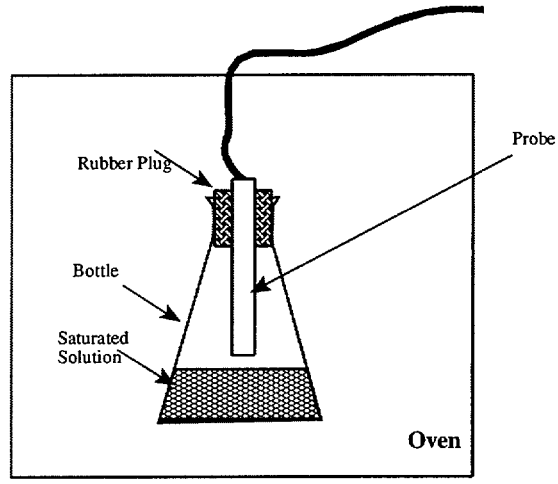

Figure 1. Apparatus used for the measurement of deliquescence relative humidity.

The conductivity cells used for measuring the conductivity of the hygroscopic salts are illustrated in Figure 2. Each cell had one or more layers of filtration paper between two platinum electrodes. The filtration paper in Type A cell had dimensions of 1 (thickness) × 3 (width) × 31 (length) mm, whereas the filtration paper for Type B cell had dimensions of 0.23 × 26 × 46 mm. Prior to the test, the filtration paper was soaked with a solution that was saturated, at the testing temperature, with the salt or salt mixtures of interest. The filtration paper is used to help form an evenly distributed layer of salt deposit between the two electrodes. It was observed in

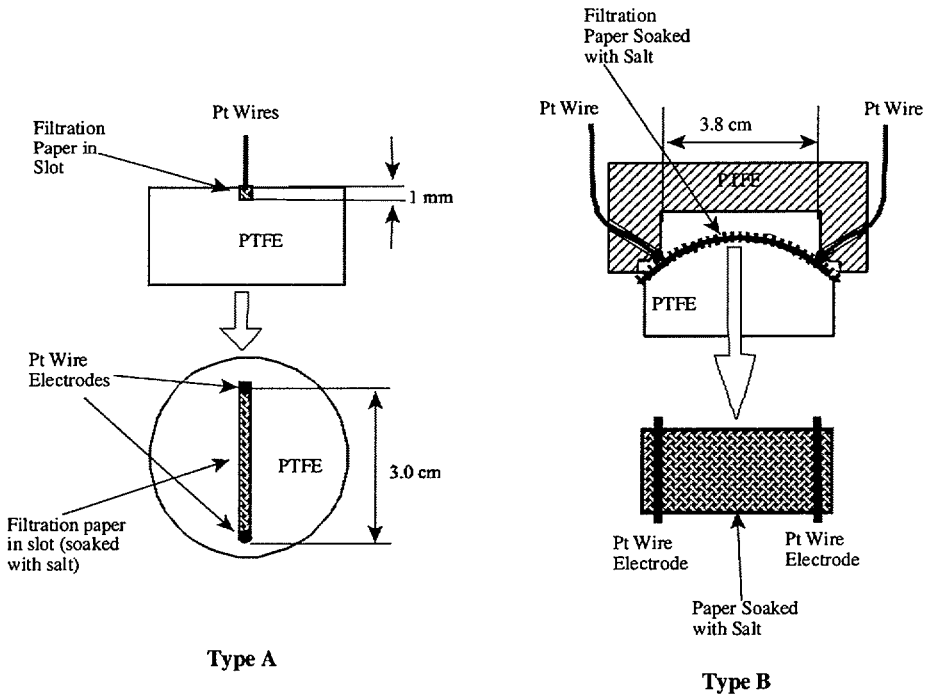

Figure 2. Schematic diagrams of the conductivity cells used in the study.

Table 1. Comparison between measured and published deliquescence relative humidity (%) for single salts

Salt	Temperature (°C)	Measured (%)	Published* (%)	Error (%)
NaCl	38.1	75.8	74.7	1.5
	48	76.8	74.5	3.1
	69	74.6	75.0	-0.5
$NaNO_3$	23	74.9	75.0	-0.1
	48	69.7	69.5	0.3
	69	62.7	66.2	-5.3
KNO_3	48	86.5	85.5	1.1
KCl	23	84.6	84.6	0.0
	38.1	81.7	82.6	-1.1
	48	78.3	81.5	-4.0
	69	82.0	79.6	3.0
	85.8	78.7	78.6	0.1
$MgCl_2$	23	33.9	32.8	3.5
	38.1	31.7	31.7	0.0
	48	31.0	30.7	1.1
	69	29.1	28.0	3.8
	85.8	25.1	25.0	0.4
99% confidence interval:				1.51

* Reference [6].

preliminary tests that salt tends to form isolated clumps during crystallization if the filtration paper was not used, which makes the measurement of conductivity unreliable. The Type A cell was used during initial tests and the Type B cell was used in later tests. The Type B cell was an improvement over the Type A cell because of its larger exposed surface area and thinner layer of paper, which allowed for quicker equilibration.

During the experiment, one or more conductivity cells were placed in a humidity chamber (Blue M Temperature/Humidity Cabinet by GS Blue M Electric). The relative humidity indicator of the chamber was calibrated using the hygrometer mentioned above. The relative humidity of the chamber was also cross-checked using the measured conductivities of pure salts (see the results section). An Electrochemical Interface (Model SI 1287, Solartron) and an Impedance/Gain-Phase Analyzer (Model SI 1260, Solartron), in conjunction with the Z-Plot software (Version 2.1, Scribner Associates), were used to measure the impedance between the two electrodes at a frequency of 1000 Hz. As the Z-Plot software only measures the impedance spectrum for one frequency cycle, a GUI-based (graphic user interface) Visual Basic program was developed for the experiment. The Visual Basic program activates the Z-Plot impedance measurement functions at a predetermined time interval (usually 1 or 5 minutes) using the Z-Plot's Object Link and Embed feature. The Visual Basic program also displays the impedance data graphically on a computer monitor and saves the data in memory as they become available from the Z-Plot program.

All solutions were prepared using 18.2 Mohm-cm deionized water and reagent grade chemicals supplied by Fisher Scientific.

RESULTS AND DISCUSSION

Deliquescence relative humidity of salt mixtures

The measured DRHs as a function of temperature are plotted in Figure 3. For comparison, the DRHs of pure salts taken from the literature [6] are also presented. The figure shows that the DRHs of salt mixtures containing Na^+, K^+, NO_3^- and Cl^- are significantly lower than those of the single salt components. The lowest DRH among the single salts is 65% at 86 °C (for $NaNO_3$), whereas the DRH of the $NaCl+NaNO_3+KNO_3$ mixture is only 43%. The latter value is significantly lower than the former, which is used as the critical relative humidity for aqueous corrosion by the DOE in its model analysis [1,4]. The lower DRH of salt mixtures compared to single salts suggests that the onset of aqueous corrosion of the drip shield/waste package may be earlier and its duration may be longer than the onset and duration that are assumed based on the DRH of a pure $NaNO_3$ salt. Also, because DRH decreases with increasing temperature, a lower DRH implies that formation of a corrosive brine and possible initiation of aqueous corrosion may occur at a temperature that is higher than is assumed based on the DRH of $NaNO_3$.

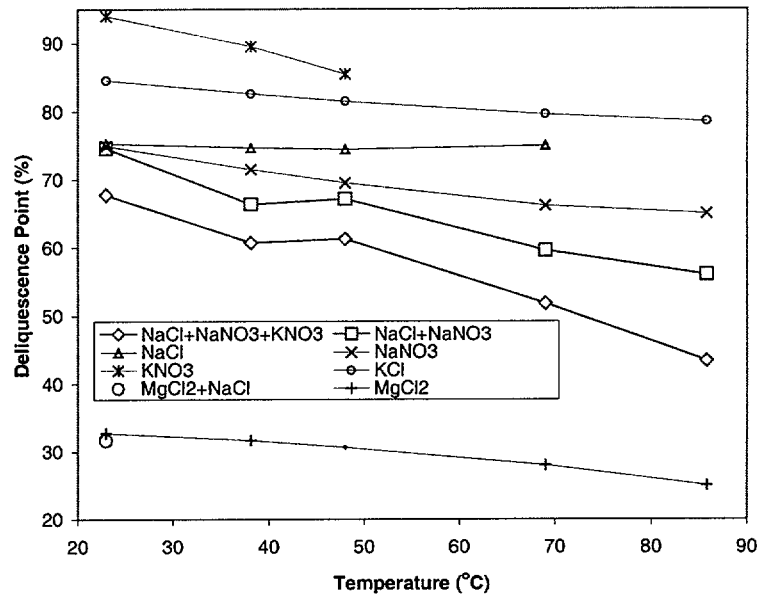

Figure 3. Comparison between the deliquescence relative humidities of pure and mixed salts. (Note: values for salt mixtures are measured; values for pure salts are from [6]).

The DRH of the $NaCl+NaNO_3+KNO_3$ system at 16.5 °C was reported to be 30.5% [7]. However, this value was not reproduced in this work. Based on the trend shown in Figure 3, the DRH for the $NaCl+NaNO_3+KNO_3$ system is likely to be 70% at 16.5 °C. This disagreement contrasts with the observed good agreement between all the measured pure salt DRH and published data (see Table 1) under the same set of conditions.

Conductivity of salt deposits

Data plotted in Figure 4 show the relationship between the

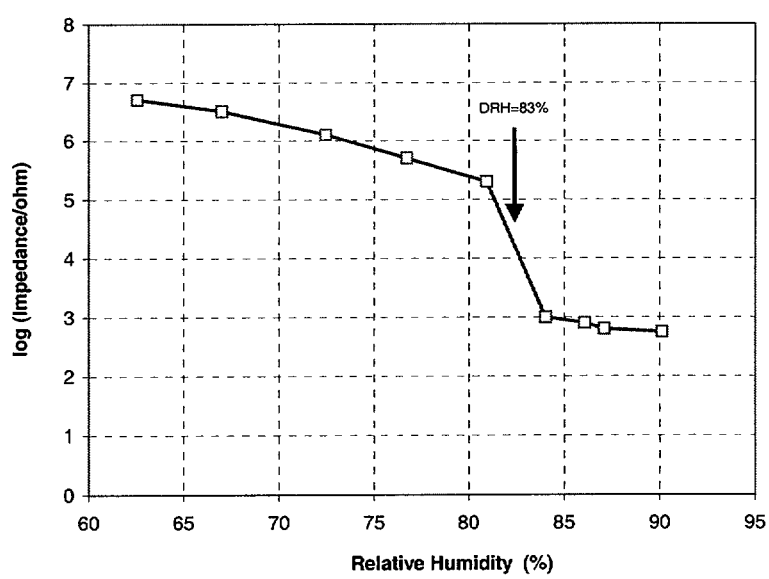

Figure 4. Data for KCl at 30 °C showing typical relationship between impedance and relative humidity.

impedance of KCl in the filtration paper and the relative humidity. At relative humidities less than 65%, the impedance was close to 1×10^7 ohm, which is the value measured with the electrodes disconnected (i.e., the upper limit of the experimental setup measuring at a 1000 Hz frequency). At a relative humidity close to 67% (or about 20% below the DRH), the impedance starts to decrease and reaches 1×10^5 ohm at a relative humidity just below the DRH. When the relative humidity is slightly above the DRH (83%), the impedance decreases dramatically to about 1×10^3 ohm.

In principle, the conductivity of the salt, λ ($ohm^{-1} \cdot m^{-1}$ or $S \cdot m^{-1}$), can be calculated according to equations (1) and (2):

$$L = 1/Z \tag{1}$$

$$L = \lambda(A/l) \tag{2}$$

where L is the conductance (ohm^{-1}), Z is the measured impedance (ohm), A the sectional area of the wetted filtration paper (thickness times width, m^2) and l is the distance between the two electrodes (m). The ratio of l/A is also called the conductivity cell constant. However, the value of A for the filtration paper is not precisely known because the conducting electrolyte layer may become thicker than the dry paper when the salt absorbs water at high relative humidities. Thus, the conductivity cell constant is not well defined. To avoid difficulties in deriving the values of conductivity, λ, the relative conductance L_R or relative conductivity λ_R of the salt is reported in this paper. The relative conductance and relative conductivity are defined as:

$$L_R = L/L^o \tag{3}$$

$$L_R = Z^o/Z \tag{4}$$

and

$$\lambda_R = \lambda/\lambda^o \tag{5}$$

In equation (3) through (5), the superscript, o, denotes the values of conductance, impedance, and conductivity measured at a relative humidity immediately above the DRH of the salt.

Substitution of equation (2) into equation (5) yields:

$$\lambda_R = L_R\ (A^o/l^o)/(A/l)] \tag{6}$$

Therefore, the numerical value of relative conductance, L_R, is identical to the relative conductivity, λ_R, if the conductivity cell constant is not affected by the relative humidity (i.e., $A/l = A^o/l^o$). In the relative humidity range below the DRH, the change in the thickness of the electrolyte layer may not be significant, even though empty spaces may be formed in the pores when water evaporates at low relative humidities. Therefore, A/l may be considered constant in this range. The relative conductance may be used as an approximation of the relative conductivity, or apparent relative conductivity, for the purpose of this work.

Figure 5 shows the relative conductance values of two single salts measured at 30 °C. As shown in the figure, the relative conductance of KCl and $NaNO_3$ increased from approximately 2×10^{-4}, which is close to the lower detection limit of the measuring system, to about 1×10^{-2} when the relative humidity changed from 20 to 55% below their DRHs to values that are slightly below their DRHs. At relative humidities about the DRH, the relative conductance became unity. The conductance of the salts requires the presence of water for the transport of ionic species. The increase in the conductance or conductivity of the salts at relative humidities lower than their DRHs implies that adsorption of water on salt particles initiates at relative humidities lower than the DRH. This observation is consistent with previous findings [8–10] on the adsorption of water on salt particles. Vogt and Finlayson-Pitts [10], using diffuse reflectance infrared Fourier transform spectrometry, observed that significant amounts of water reside on the surface of a pure NaCl aerosol surface at a relative humidity of 53.8%, far below its DRH of 75.7%.

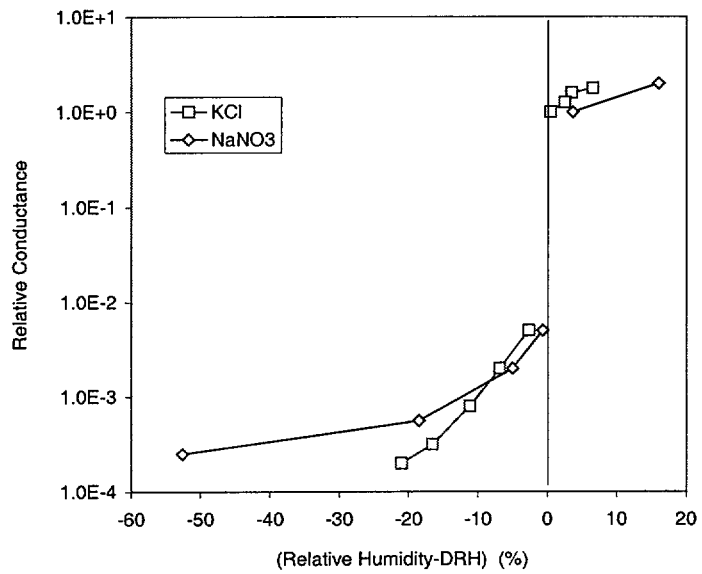

Figure 5. Measured relative conductance of KCl and $NaNO_3$ as a function of the difference between the relative humidity and the deliquescence relative humidity at 30 °C. Note: Type A Cell was used.

Other similar experiments were conducted at 50 °C and the data are presented in Figure 6. The variations in the relative conductance at a given difference between the relative humidity and the DRH of the different types of salts are probably due to variations in the particle size, porosity, surface roughness and hydrophilic properties of the salts. Although not a sufficient condition, the presence of water is a necessary condition for aqueous corrosion to take place. It is not known from the experiments how much water was adsorbed at the time conductivity started to increase. It has been reported that aqueous films thicker than three monolayers possess properties that are close to those of bulk water [11]. The increase in relative conductance as shown in Figures 5 and 6 also implies that aqueous corrosion might take place at a relative humidity that is 20% lower than the DRH of the salt deposits.

Simulation by the DOE [12] shows that after emplacement of nuclear waste packages in the proposed repository, the temperature of the waste package may increase to about 100 °C, and then decrease during the ventilation period. Upon closure of the drift, the temperature of the waste package again may increase sharply to 160 °C. The minimum relative humidity that corresponds to the 160 °C peak temperature is about 20%. According to the DOE salt/precipitate analysis, it is likely that the salt deposit on the waste package/drip shield would be a mixture containing NaCl, $NaNO_3$ and KNO_3 [1]. As the DRH of this mixture is expected to be significantly lower than the DRH of pure $NaNO_3$ salt and if aqueous corrosion starts at relative humidities 20% below the DRH, aqueous corrosion may take place during the entire

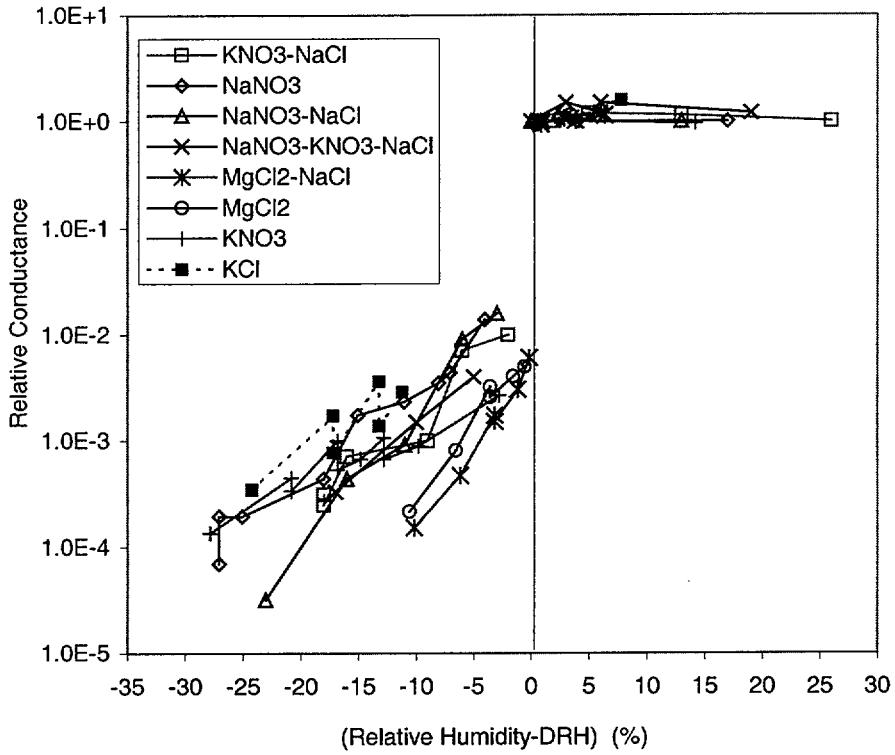

Figure 6. Measured relative conductance of salts as a function of the difference between the relative humidity and the deliquescence relative humidity of the salts at 50 °C. Note: Type B Cell was used.

emplacement period. Therefore, the critical relative humidity used by the DOE may not be realistic.

CONCLUSIONS

The relative conductivity of salt mixtures containing Na^+, K^+, NO_3^- and Cl^- at different relative humidities and the DRHs of these salts were measured experimentally. Measured DRH values show that at 86 °C , the DRH of the salt mixture containing NaCl, $NaNO_3$ and KNO_3 is significantly lower than the critical DRH used by the DOE based on the DRH of $NaNO_3$. The results from this study show that as the relative humidity increases, the conductivity of a dry salt or salt mixture starts to increase at a humidity value that is significantly lower than the DRH of the salt or salt mixture. This increase in conductivity implies that initiation of drip shield or waste package aqueous corrosion may occur at a relative humidity significantly lower than the DRH of the salt mixture deposited on them. Thus, aqueous corrosion may occur earlier, its duration may be longer, and the temperature at which it occurs may be higher than predicted by the DOE based on the DRH of a pure salt.

ACKNOWLEDGMENTS

This paper was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Material Safety and Safeguards, Division of Waste Management, under Contract No. NRC-02-97-009. The paper is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC. Technical discussions with G.A. Cragnolino, D.S. Dunn, C.S. Brossia, N. Sridhar and V. Jain are gratefully appreciated.

REFERENCES

1. Civilian Radioactive Waste Management System Management and Operating Contractor, "Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier," ANL–EBS–MD–000001, Revision 00 ICN 01, (Las Vegas, NV, Office of Civilian Radioactive Waste Management System, Management and Operating Contractor, 2000).
2 R. T. Pabalan, L. Yang and L. Browning, "Deliquescence Behavior of Multicomponent Salts: Effects on the Drip Shield and Waste Package Chemical Environment at the Proposed Nuclear Waste Repository at Yucca Mountain, Nevada", Scientific Basis for Nuclear Waste Management XXV (MRS meeting, Boston, MA, 2001).
3. C.S. Brossia, L. Browning, D.S. Dunn. O.C. Moghissi, O. Pensado and L. Yang. "Effect of Environment on the Corrosion of Waste Package and Drip Shield Materials," CNWRA 2001-003 (San Antonio, TX: Center for Nuclear Waste Regulatory Analyses, 2001).
4. Civilian Radioactive Waste Management System Management and Operating Contractor, "Waste Package Degradation Process Model Report," TDR-WIS-MD-000002 Revision 00 ICN 02 (Las Vegas, NV, Office of Civilian Radioactive Waste Management System, Management and Operating Contractor, 2000).
5. ASTM Designation: E104–85 (Reapproved 1996), "Standard practice for maintaining constant relative humidity by means of aqueous solutions standard" (1996).
6. L. Greenspan, J. of Research of the National Bureau of Standards. **81A**, 89–96 (1977)
7 R.C. Weast, ed. 1981. CRC Handbook of Chemistry and Physics. 62nd Edition. (CRC Press, 1974), p. E-46.
8. Z. Ge, A. S. Wexler, and M. V. Johnston, J. Phys. Chem., **102**, 173–180 (1998).
9 M.D. Cohen, R.C. Flagan, J.H. Seinfeld, J. Phys. Chem., **91**, 4575 (1987).
10 R. Vogt and B.J. Finlayson-Pitts, J. Phys. Chem., **98**, 3747 (1994).
11 C. Leygraf and T. Graedel, "Atmospheric Corrosion" (Wiley Interscience, New York, 2000), Chapter 2.
12. Civilian Radioactive Waste Management System Management and Operating Contractor, "Total System Performance Assessment for the Site Recommendation", TDR-WIS-PA-000001, Revision 00 ICN 01 (Las Vegas, NV, Office of Civilian Radioactive Waste Management System, Management and Operating Contractor, 2000).

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ATTN: Mrs. Deborah A. DeMarco
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Program Management, Policy Development, and Staff
Office of the Director
Mail Stop 8D–37
Washington, DC 20555

Subject: Programmatic Review of Poster

Dear Mrs. DeMarco:

The enclosed poster is being submitted for programmatic review. This poster will be submitted for presentation at the Materials Research Society Annual meeting, to be held November 26–29, 2001, in Boston, Massachusetts. The title of this poster is:

> "Experimental Determination of the Deliquescence Relative Humidity and Conductivity of Multicomponent Salt Mixtures"
> by Lietai Yang, Roberto T. Pabalan, and Lauren Browning

This poster a product of the CNWRA and do not necessarily reflect the view(s) or regulatory position of the NRC.

Please advise me of the results of your programmatic review. Your cooperation in this matter is appreciated.

Sincerely,

Budhi Sagar
Technical Director

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Washington Office • Twinbrook Metro Plaza #210
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

Experimental Determination of the Deliquescence Relative Humidity and Conductivity of Multicomponent Salt Mixtures

Lietai Yang, Roberto T. Pabalan and Lauren Browning
Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, Texas, U.S.A.

INTRODUCTION

Deposition of aerosol and dust from ventilation air and evaporation of water seeping into the drift of a proposed geologic repository at Yucca Mountain, Nevada, may lead to the accumulation of hygroscopic salts on drip shield and waste package surfaces [1]. These hygroscopic salts will sorb moisture from the atmosphere and form brine solutions, potentially causing aqueous corrosion of the drip shield and waste package. The U.S. Department of Energy (DOE) performance assessment model assumes that aqueous corrosion of waste package and drip shield begins when the relative humidity reaches the deliquescence relative humidity (DRH) of pure $NaNO_3$ salt in the temperature range that was predicted for the geological repository system [2]. Aqueous corrosion requires the presence of an electrolyte that is conductive to ionic species. In this study, the relative values of ionic conductivity of various salts were measured as a function of relative humidity at constant temperatures. The minimum relative humidity at which conductivity starts to rise was compared to the DRH of the salt. Also, because DRH data for salt mixtures containing Na^+, K^+, NO_3^- and Cl^- are not available from the literature, these were experimentally determined at the same temperatures as the conductivity tests.

EXPERIMENTAL

Deliquescence Relative Humidity Measurement

The DRH of salt mixtures was measured using a hygrometer (Model 4085CC, Control Company, TX, USA). The test set-up is shown in Figure 1(a). The measurement was conducted according to the procedures given by the ASTM standard E-104. Both the glass flask and the hygrometer were placed in an oven (Model 838F, Fisher Scientific) and held at a constant temperature for at least 30 minutes before each measurement was made. During the experiment, identical glass flasks containing pure salt solutions of NaCl, $NaNO_3$, KNO_3, KCl and $MgCl_2$ were also placed in the oven and used as controls for verifying and correcting the hygrometer readings based on their DRH values published in the literature[3].

Conductivity Measurement

The conductivity cells used for the measurement of the conductivity of the hygroscopic salts are illustrated in Figure 1(b). One or more layers of filtration paper are placed between the two platinum electrodes. Prior to the test, the filtration paper was soaked with a solution that is saturated, at the testing temperature, with the salts or salt mixtures to be tested. The filtration paper helps the salt form an evenly distributed layer between the two electrodes to simulate the salt deposit. During the experiment, one or more conductivity cells are placed in a humidity chamber (Blue M Temperature/Humidity Cabinet by GS Blue M Electric). The relative humidity indicator of the humidity chamber was calibrated using the hygrometer mentioned above. The relative humidity of the chamber is also cross-checked by the measured conductivities of pure salts (see the results section). An Electrochemical Interface (Model SI 1287, Solartron) and an Impedance/Gain-Phase Analyzer (Model SI1260, Solartron), in conjunction with the Z-Plot software (Version 2.1, Scribner Associate), were used to measure the impedance between the two electrodes at a frequency of 1000 Hz.

RESULTS

Deliquescence relative humidity of salt mixtures

The measured DRHs as a function of temperature are plotted in Figure 2. For comparison, the DRHs of pure salts taken from the literature [3] are also presented. The figure shows that the DRHs of salt mixtures containing Na^+, K^+, NO_3^- and Cl^- are significantly lower than those of the single salt components. The lowest DRH among the single salts is 65% at 85.8 °C (for $NaNO_3$), whereas the DRH of the $NaCl+NaNO_3+KNO_3$ mixture is only 43%. The latter value is significantly lower than the former, which is used as the critical relative humidity for aqueous corrosion by the DOE in its model analysis [2]. The lower DRH of salt mixtures compared to single salts suggests that the onset of aqueous corrosion of the drip shield/waste package may be earlier, its duration may be longer, and the temperature at which it occurs may be higher than assumed based on the DRH of a pure $NaNO_3$ salt.

Conductivity of salt deposits

Figure 3(a) shows typical responses of the impedance between the two electrodes to changes in relative humidity. The filtration paper was soaked with saturated KCl solution. The data shown in the figure were measured at 30 °C using three frequencies. A frequency of 1000 Hz was selected for further measurements of the conductivity behavior of salt deposits.

The data plotted in Figure 3(b) show the relationship between the impedance of KCl in the filtration paper and the relative humidity. At relative humidities less than 65%, the impedance was close to 1×10^7 ohm, which is the the upper limit of the measurement system at 1000 Hz frequency. At a relative humidity close to 67% (or about 20% below the DRH), the impedance starts to decrease and reaches 1×10^5 ohm at a relative humidity just below the DRH. When the relative humidity is slightly above the DRH (83%), the impedance decreases steeply to about 1×10^3 ohm.

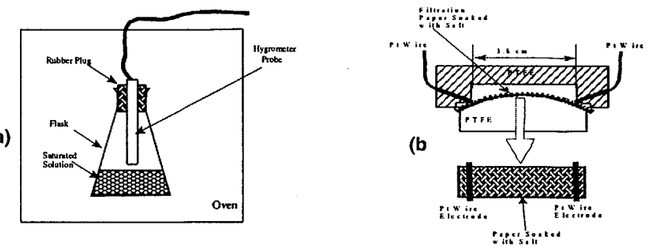

Figure 1. Schematic diagrams of the experimental apparatus for measurement of (a) deliquescence relative humidity and (b) conductivity of salt deposits.

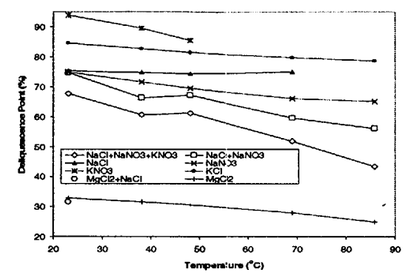

Figure 2. Comparison of the deliquescence relative humidities of pure and mixed salts.
Note: Values for salt mixtures are measured; values for pure salts are from literature [3].

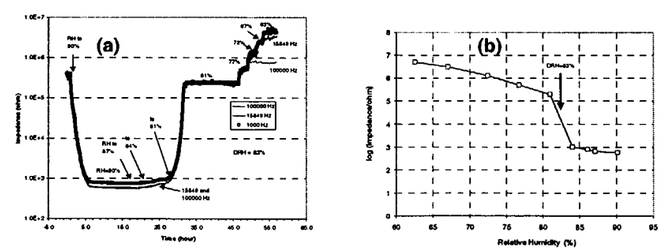

Figure 3. (a) Typical responses of impedance to changes in relative humidity (data for KCl deposit); (b) relationship between impedance and relative humidity.

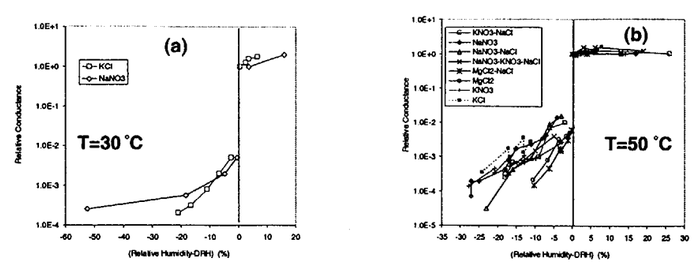

Figure 4. Measured relative conductance of salts as a function of the difference between the relative humidity and the DRH at (a) 30 °C and (b) 50 °C.

RESULTS (Cont'd.)

In principle, the conductivity of the salt can be calculated from the measured impedance. However, the conductivity cell constant is not precisely known because the conducting electrolyte layer may become thicker than the dry paper when the salt absorbs water at high relative humidities. To avoid difficulties in deriving the values of conductivity, relative conductance (L_R) or relative conductivity (λ_R) of the salt is reported in this paper. The relative conductance and relative conductivity are defined as:

$$L_R = L/L^\circ \quad (1)$$

$$\lambda_R = \lambda/\lambda^\circ \quad (2)$$

In Equations (1) and (2), the superscript, °, denotes the values of the conductance and conductivity at a relative humidity immediately above the DRH of the salt. The numerical value of L_R is identical to λ_R if the conductivity cell constant is not affected by the relative humidity. In the relative humidity range below the DRH, the cell constant may be considered constant and the relative conductance may be used as an approximation of the relative conductivity. Figure 4(a) shows the relative conductance of two single salts measured at 30 °C. As shown in the figure, the relative conductance of the salts increased from approximately 2×10^{-4} to about 1×10^{-2} when the relative humidity changed from 20 to 55% below their DRHs to values that are slightly below their DRHs. At relative humidities about the DRH, the relative conductance became unity. Other similar experiments were conducted at 50 °C and the data are presented in Figure 4(b).

Conductance of the salts requires the presence of water for transport of ionic species. The increase in the conductance or conductivity of the salts at relative humidities lower than their DRHs implies that adsorption of water on salt particles initiates at relative humidities lower than the DRH. Although not a sufficient condition, the presence of water is required for aqueous corrosion to occur. It is not known from this experiment how much water was adsorbed at the time the conductivity started to increase. It has been reported that aqueous films thicker than three monolayers possess properties that are close to those of bulk water [4]. The increase in relative conductance as shown in Figure 4 also implies that aqueous corrosion might take place at a relative humidity that is 20% lower than the DRH of the salt deposits.

Simulation by the DOE [5] shows that after emplacement of nuclear waste packages in the proposed repository, the temperature of the waste package surface may increase to about 100 °C, and then decrease during the ventilation period. Upon closure of the drift, the temperature of the waste package surface may increase sharply again to 160 °C. The minimum relative humidity that corresponds to the 160 °C peak temperature is about 20%[5]. If aqueous corrosion starts at relative humidities 20% below the salt mixture's DRH, which is significantly lower than the DRH values of pure salts, aqueous corrosion may take place during much of the emplacement period. Therefore, the critical relative humidity used by the DOE may not be conservative.

CONCLUSIONS

The relative conductivity of salt mixtures containing Na^+, K^+, NO_3^- and Cl^- at different relative humidities and the DRH of these salts were measured experimentally. Measured DRH values show that at 86 °C, the DRH of the salt mixture containing NaCl, $NaNO_3$ and KNO_3 is significantly lower than the critical DRH used by the DOE based on the DRH of $NaNO_3$. The results from this study show that as the relative humidity increases, the conductivity of a dry salt or salt mixture starts to increase at a humidity value that is significantly lower than the DRH of the salt or salt mixture. This increase in conductivity implies that initiation of drip shield or waste package aqueous corrosion may occur at a relative humidity significantly lower than the DRH of the salt mixture deposited on them. Thus, the initiation time for aqueous corrosion is earlier and the duration is longer than predicted by the Department of Energy based on the DRH of a pure salt.

REFERENCES

(1) C.S. Brossia, L. Browning, D.S. Dunn, O.C. Moghissi, O. Pensado and L. Yang, "Effect of Environment on the Corrosion of Waste Package and Drip Shield Materials," CNWRA 2001-003 (San Antonio, TX: Center for Nuclear Waste Regulatory Analyses, 2001); (2) Civilian Radioactive Waste Management System Management and Operating Contractor, "Waste Package Degradation Process Model Report," TDR-WIS-MD-000002 Revision 00 ICN 02 (Las Vegas, NV, Office of Civilian Radioactive Waste Management System, Management and Operating Contractor, 2000); (3) L. Greenspan, J. of Research of the National Bureau of Standards. 81A, 89–96 (1977); (4) C. Leygraf and T. Graedel, "Atmospheric Corrosion" (Wiley Interscience, New York, 2000), Chapter 2; (5) Civilian Radioactive Waste Management System Management and Operating Contractor, "Total System Performance Assessment for the Site Recommendation", TDR-WIS-PA-000001, Revision 00 ICN 01 (Las Vegas, NV, Office of Civilian Radioactive Waste Management System, Management and Operating Contractor, 2000).

ACKNOWLEDGMENTS

This poster was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Material Safety and Safeguards, Division of Waste Management, under Contract No. NRC-02-97-009. The poster is an independent product of CNWRA and does not necessarily reflect the views or regulatory position of the NRC. Technical discussions with G.A. Cragnolino, D.S. Dunn, C.S. Brossia, N. Sridhar and V. Jain are gratefully appreciated.