SRNL-STI-2010-00409, REVISION 0

Key Words:
Stress corrosion cracking
304L Stainless Steel
Relative Humidity

Retention: Permanent

RELATIVE HUMIDITY TESTS IN SUPPORT OF THE 3013 STORAGE AND SURVEILLANCE PROGRAM

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AUGUST 2011

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Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-08SR22470

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Printed in the United States of America

Prepared for
U.S. Department of Energy

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LIST OF ACRONYMS AND UNITS

atm	Atmosphere
std cc/sec	standard cubic centimeters per second
IC	Ion Chromatography
ICPES	Inductively Coupled Plasma Emission Spectroscopy
LANL	Las Alamos National Laboratory
M&TE	Measurement and Test Equipment
NAA	Neutron Activation Analysis
ND	Not Determined
OD	Outside Diameter
RH	Relative Humidity
SCC	Stress Corrosion Cracking
SRNL	Savannah River National Laboratory

1.0 EXECUTIVE SUMMARY

Techniques to control the initial relative humidity over oxide/salt mixtures have been developed using cerium oxide as a surrogate for plutonium oxide. Such control is required to validate certain assumptions in the Department of Energy Standard DOE-STD-3013, and to provide essential information to support field surveillance at the storage sites for excess plutonium oxides. Concern over the validity of the assumption that corrosion induced degradation in 3013 containers could be controlled by assuring that the moisture content of any stored oxide/salt mixture was below 0.5 w t% arose when stress corrosion cracks were found in test samples exposed at room temperature to plutonium oxide/salt mixtures having a moisture content only marginally above 0.5 wt %. Additionally, analysis of the stress corrosion cracking observations suggests that the initial relative humidity over the oxide/salt mixture may play a major role in the cracking process.

The investigations summarized in this report provide the procedures necessary to control the initial relative humidity to selected values within the range of 16 to 50% by controlling the loading relative humidity (18 to 60%) and the oxide/salt mixture water content (0.05 to 0.45 wt %). The studies also demonstrated that the initial relative humidity may be estimated by calculations using software EQ3/6. Cerium oxide/salt mixtures were used in this study because qualification tests with non-radioactive materials will reduce costs while increasing the breadth of the test programs required to support field surveillances of stored 3013 containers.

2.0 INTRODUCTION

The integrated surveillance program for packaged 3013 containers is partially supported by shelf-life testing programs and other studies that are conducted to validate assumptions used in the Department of Energy Standard, DOE-STD-3013, and to provide essential information to complement field surveillances at the storage sites for excess plutonium oxide materials [1, 2]. The primary goal of the surveillance program is to provide confidence that material stabilized and packaged to meet the DOE standard can be stored safely for 50 years. The shelf-life testing program includes small-scale and full-scale experiments that provide essential data on gas generation and corrosion for bounding and representative storage conditions. Other supporting studies are also initiated as emergent results from shelf-life testing indicate concerns relevant to the 3013 storage inventory.

One specific corrosion concern identified in previous small-scale experiments was stress corrosion cracking (SCC) of welded Type 304L stainless steel test coupons. The teardrop coupons cracked while exposed at room temperature to a plutonium oxide/salt mixture with a bounding (0.5 wt %) water content [3]. Such cracking was not anticipated; so a test plan was developed and enacted to address the potential for SCC in the inventory of 3013 containers in K-Area and other storage sites [2]. Analysis of the SCC data suggested that deliquescence of salts in the oxide/salt mixtures was a precursor to crack initiation and propagation. Therefore, further testing was designed, in part, to assess the threshold relative humidity (RH) at which SCC will occur in both small-scale and full-scale experiments. Clearly, such an assessment necessitates an ability to control the initial relative humidity when packaging oxide/salt mixtures.

Techniques to control the initial relative humidity over oxide/salt mixtures were developed using cerium oxide as a surrogate for plutonium oxide to eliminate the experimental difficulties and cost associated with handling radioactive materials. It is anticipated that the techniques and protocols developed will be applicable to radioactive materials with the inclusion of radiological safety procedures.

This report describes a series of experiments conducted to determine the initial relative humidity inside a closed small-scale test cell as a function of the loading relative humidity and the oxide/salt-mixture water content. These experiments with non-radioactive materials were conducted relatively rapidly and were more economical than tests using plutonium oxides, thus many parametric values were examined in a relatively short time. The test results were used to establish the loading protocol for achieving a targeted initial relative humidity in the radioactive test cells where plutonium oxide/salt mixtures are used.

The test results showed that a range of initial relative humidity (16-50%) could be obtained depending on the loading relative humidity (18-60%) and oxide/salt mixture water content (0.05-0.45 wt %).

3.0 EXPERIMENTAL DESCRIPTION AND TASK ACTIVITIES

This experimental work described in the report consisted of determining the initial RH in the small-scale test cell as a function of the oxide/salt mixture water content and loading RH. This work is part of Task II.B.1 of the 3013 container SCC test plan [2]. Cerium oxide was used as a replacement for plutonium oxide in the oxide/salt mixtures. The oxide/salt mixture used in these experiments was prepared to have a composition similar to the oxide/salt mixtures stored in 3013 containers except that the oxide was cerium rather than plutonium. The special test cells fabricated and used for the relative humidity studies were of a similar design to those previously used in the small-scale corrosion tests [3] that produced the stress corrosion cracks in the teardrop coupons. The cells will be referred to as humidity cells since relative humidity was the primary parameter of interest. The humidity probes and thermocouples were attached to each cell and were calibrated prior to testing. The procedure of loading the test cells was standardized as much as possible to minimize the influence of procedural error on these measurements. The experimental details are described in the following sections of this report.

3.1 OXIDE/SALT MIXTURE PREPARATION

The oxide/salt mixture used for the entirety of this testing had a composition of 98 wt % CeO_2, 0.85 wt % NaCl, 0.85 wt % KCl, and 0.3 wt % $CaCl_2$. This composition was selected to duplicate that used when SCC was observed previously in small-scale corrosion tests [3]. Special anhydrous forms of the chloride salts were procured and the cerium oxide was prepared at SRNL by calcining cerium oxalate at temperatures of approximately 750 °C. Prior to its use for this testing the cerium oxide was heated at 950 °C for two hours. The master batch (500 g) of the oxide/salt mixture was prepared in early 2009.

Most of the steps in this process were performed in an argon-inert glovebox, where humidity levels were generally below 500 ppm (the maximum was 700 ppm), which corresponds to a relative humidity of 1–2% at 25 °C. Several of the preparation steps required heating the oxide, the salt mixtures or the oxide/salt mixtures. Heating was accomplished out of the glovebox and the materials to be heated were transported from the glovebox to the argon-inert furnace in covered quartz crucibles in a desiccator. The quartz crucibles were used for all heating steps and were removed from the desiccator before the heating was initiated. After heating, the material was cooled to 300 °C before placing back into a desiccator to cool to room temperature. The desiccator was vented through a desiccant filter to minimize moisture uptake and was returned to the argon-inert glovebox prior to opening.

The mixture of sodium, potassium and calcium chloride salts was prepared prior to combining with the cerium oxide. The requisite quantity of each salt was weighed and the salts were mixed together. The balance and calibrated weight set were compliant with M&TE controls. The salt mixture was heated to 825 °C for fifteen minutes after which the salts were visually confirmed to have melted. Pre- and post-heating weight measurements of the salt mixture showed a difference of approximately 0.15%. The fused salts were ground with a mortar and pestle before combining with the cerium oxide.

The oxide/salt mixture was prepared by weighing the requisite quantities of the oxide and previously prepared salt mixture and blending these quantities together using a mortar and pestle. The blended oxide/salt mixture was heated for 30 minutes at 825 °C, cooled to room temperature, transported to the argon-inert glove box and then ground until fine. During the grinding step approximately 2% of material was lost. Several small batches of the oxide/salt mixture were prepared and then combined and mixed to make the master batch. The master batch was stored in the argon-inert glovebox and portions of the batch were used, as needed, in the test program.

3.2 HUMIDITY CELL CONFIGURATION

The humidity cells, Figure 3.2.1, were of similar design to those used for the small scale tests that showed stress corrosion cracking. These cells will be used again to complete the remaining small-scale tests specified in the 3013 container SCC test plan [2]. The bottom section of the cell is approximately 2 in OD and 2.5 in tall and is basically a flange with a welded bottom. The o-ring, chain clamp and flanges were procured from EVAC AG. The lid flange had Swagelok fittings welded in place for the thermocouple and humidity probe. The cell body is fabricated from 304L stainless steel. The humidity probes and thermocouples were supplied by EdgeTech and Omega, respectively. The dish to hold the oxide/salt mixture was made of borosilicate glass.

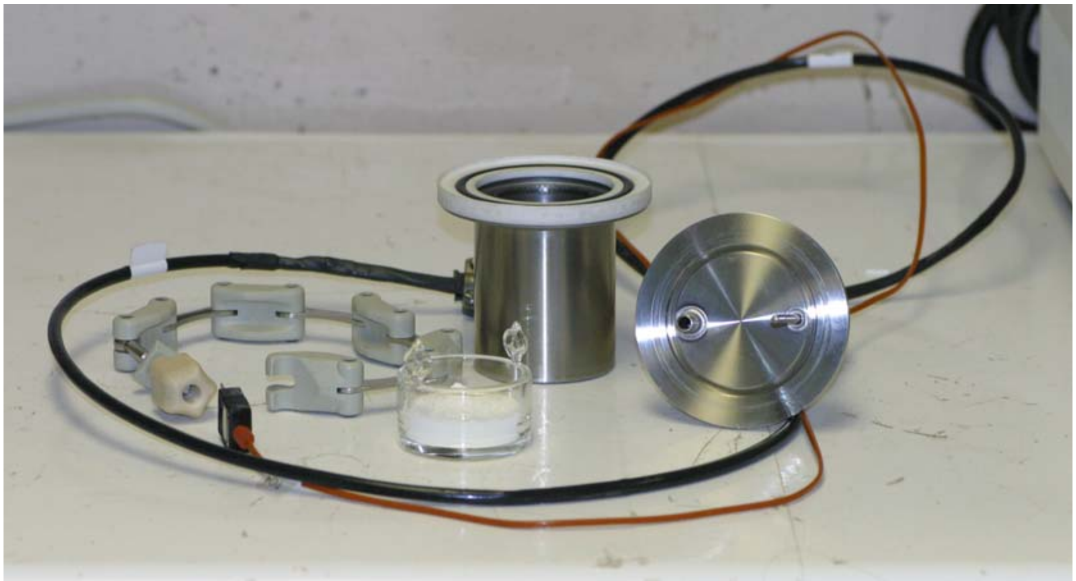

Figure 3.2-1 Components of humidity cells include flanged top with an Omega thermocouple and an EdgeTech humidity probe, flanged bottom, EVAC o-ring, EVAC chain clamp, and salt dish.

The cell components were helium leak tested for leak tightness. The cell bodies without the humidity probe passed the leak test and showed a rate of helium leakage of 10^{-9} std cc/sec at a pressure of 1 atm. However, placement of the humidity probes generally increased the leakage and caused the leak rates to vary between 10^{-3} to 10^{-9} std cc/sec. Several attempts were made to seal the probes with epoxy but these attempts were of limited success.

3.3 HUMIDITY PROBE AND THERMOCOUPLE CALIBRATION

Each humidity probe and thermocouple was calibrated prior to the start of testing. The thermocouples were checked using a Hart Scientific, Model 9107, dry-well calibrator (M&TE) over the temperature range of 10-90 °C. The thermocouples were allowed to equilibrate to a set point for approximately two hours. When the set point was either 20 or 30 °C, the thermocouple values varied from the set point by 0.3 to 0.6 °C and at temperatures above 50 °C, the variation from the set point was up to 2 °C.

The humidity probes were calibrated using a programmable chilled mirror chamber supplied by EdgeTech with a RH accuracy of 0.5 % over the range of 5-95 % (RH CAL portable humidity calibrator). Several probes were inserted into the chamber simultaneously and tested over a RH range of 5-75 % at a temperature of 25 °C. Probes were allowed to stabilize at each humidity level for at least 1.5 hours (usually between 2 and 3 hours). The probes were checked both before and after testing. Figure 3.3-1 shows the before and after calibration curves for one of the four probes used during testing. The calibration curves for the other three probes were similar.

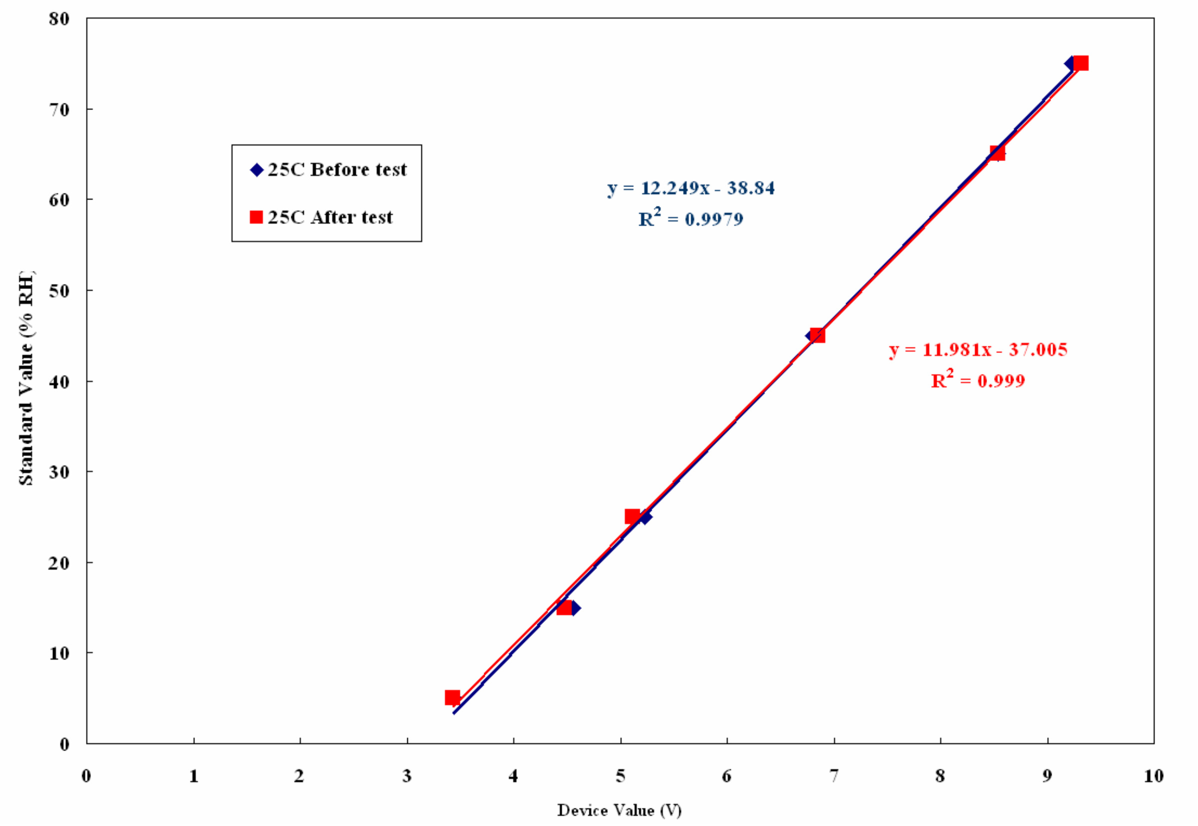

Figure 3.3-1 Calibrations curves for humidity probe before and after use in the non-radioactive humidity testing.

A measure of the RH variability for each probe was calculated by averaging four measured RH values at each set point plus or minus the 95% confidence limits for those four measurements. Two measurements were made before testing and two after testing. The Standard RH is the set point plus or minus the stated RH uncertainty per the manufacturer. These data are presented in Table 3.3-1 for four probes used during this testing. In most cases the mean measured values overlap with the Standard RH values within the stated uncertainties.

Table 3.3-1 Confidence Limits for RH Measurements

Standard RH (%)	**Mean RH (%) ± 95 % Confidence Level**			
	Probe 1	**Probe 2**	**Probe 3**	**Probe 4**
5.0 ± 0.5	2.9 ± 1.0	4.4 ± 0.8	3.3 ± 0.2	3.1 ± 0.2
15.0 ± 0.5	16.9 ± 0.9	16.4 ± 0.1	16.5 ± 1.0	16.0 ± 0.1
25.0 ± 0.5	25.8 ± 0.5	24.2 ± 0.6	24.5 ± 1.2	25.5 ± 1.8
45.0 ± 0.5	45.7 ± 1.1	45.7 ± 1.3	44.8 ± 0.6	45.9 ± 0.6
65.0 ± 1.0	64.8 ± 0.3	66.1 ± 0.6	65.7 ± 0.1	65.9 ± 0.5
75.0 ± 1.0	74.4 ± 0.5	75.0 ± 1.7	74.7 ± 1.0	74.2 ± 1.2

3.4 PROCEDURE FOR LOADING HUMIDITY CELLS

A standardized procedure was developed for loading water onto the oxide/salt mixture and sealing the loaded mixture into the test cell. These tests took place in mid 2010, approximately one year after the oxide/salt mixture was made. Loading was conducted in a helium-atmosphere glove bag equipped with a Mettler (AE240) analytical balance for monitoring the oxide/salt mixture weight change. The balance was calibrated and controlled as M&TE. The balance was checked at the start of each loading using an M&TE weight set (10, 50, and 100 g) and before each measurement with the 50-g weight from that set.

The humidity in the glove bag was controlled by independently adjusting the flow rate of a moist and dry helium stream. Dry helium from the cylinder was split into two streams that had independent flow valves. One of the split streams of helium passed over a humidifying membrane, while the other stream was unaltered. After the one stream was humidified, the two streams were recombined into a single stream prior to entry into the glove bag. The humidity of the recombined stream was determined by passing a side stream over a chilled mirror humidity unit. The flow of each stream was independently controlled to obtain the desired humidity in the helium entering the glove bag. A separate humidity probe was in the glove bag to monitor changes in the bag humidity. The bag was at room temperature and the specific temperature was not controlled independently.

The salt/oxide mixture to be placed in the glove bag had been prepared and stored for approximately a year, inside an argon-inert glove box. The stored mixture was contained in a glass jar which was closed with ground glass stopper. Approximately 20 g of the salt/oxide mixture from the jar was weighed into a glass dish. A maximum of four dishes were prepared at any one time. The dish/mixture weight was measured on a Mettler analytical balance, which was controlled as M&TE. The weighed dish/mixtures were placed in a desiccator then transported to the glove bag under an argon atmosphere. The desiccator was placed into the glove bag and not opened for a minimum of two hours to assure that the helium flow into the glove bag had removed the oxygen and converted the atmosphere to dry helium.

Initially, in the glove bag each dish was removed from the desiccator in a dry helium environment (2% relative humidity), weighed, and then placed back into the desiccator. These "glove bag" weights on average were larger by approximately 0.011 g from those measured in the argon glovebox. The desired loading humidity was then obtained in the glove bag and water was generally loaded to 0.1% of the oxide/salt mixture weight by monitoring the weight change of the dish on the balance. The dish was then closed into the test cell and the relative humidity of the cell atmosphere monitored.

The relative humidity of the cell atmosphere generally decreased and after it became stable the cell was placed back into the glove bag and additional water was loaded on the oxide/salt mixture. The following steps were used for the additional water loadings. The relative humidity of the helium environment in the glove bag was adjusted to be equivalent to the stable environment developed in the test cell. The test cell was then opened in the glove bag and the dish was weighed to note any change in water content during humidity stabilization. The cell was then closed and the bag humidity was changed to be equivalent to the initial loading RH. The test cell was then reopened and the oxide/salt mixture was allowed to gain moisture to the desired level which was generally 0.25 or 0.4 wt % water. After the water loadings, the helium-filled humidity cells were stored in air at room temperature although several tests were performed at 35 and 50 °C by placing the test cells into a small oven. The cells remained closed for times ranging from 0.5 to 6 days.

3.5 CHEMICAL ANALYSIS OF OXIDE/SALT MIXTURE

The composition of the oxide/salt mixture was analyzed using different preparations and several analytical techniques. Mixture samples were analyzed as a dry powder, as a leachate, and as a solution after completely dissolving the mixture. The dry powder was analyzed using X-ray diffraction (XRD) under an inert atmosphere to prevent formation of hydrates of the chloride salts. Leachates of the mixture were produced by exposing approximately 1 g of the mixture to a small volume of distilled water (10 or 20 mL). The total time of exposure for the leachate samples was not documented but exceeded 24 hours. The leachates were analyzed using ion chromatography (IC) and neutron absorption activation (NAA, after humidity tests only) for chloride species and ion coupled plasma emission spectroscopy (ICPES) for cation concentrations.

Two methods of dissolving the mixture were used to produce the solutions for analysis. The first method, which is referred to as the nitric acid method, dissolved 0.25 g of the mixture in 30 mL of 12 M HNO_3 with 0.2 M HF. The dissolution was accomplished by exposing the mixture to the solvent for three hours at 95 °C. After dissolution 2.5 mL of 0.9 M boric acid was added to the solution to complex the fluorides. The solution volume was adjusted back to 30 mL, and then filtered through a 0.45-µm membrane filter. The analyzed solution was prepared by adding 3 mL of dissolution solution to 7 mL of de-ionized water. The second method for preparing a solution, which is referred to as the sulfuric acid method, involved dissolving approximately 0.1 g of the mixture in 5 mL of concentrated sulfuric acid mixed with 15 mL of 30% hydrogen peroxide and heating to boiling. This second method was developed since the analytical results obtained using the nitric acid method were not in good agreement with expected values. Both methods for preparing the solutions were performed in open containers. ICPES and IC were used to analyze the solutions.

4.0 HUMIDITY TEST RESULTS

These results of the non-radioactive humidity tests include chemical analysis of the fused salts and oxide/salt mixture, analysis of the oxide/salt mixture weight changes during the humidity tests and evaluation of the humidity changes in the test cells after loading.

4.1 CHEMICAL ANALYSIS

The chemical analyses of the fused salts and oxide/salt mixture were performed immediately after production and subsequently, after a humidity test. Immediately after production, samples of the fused salts were dissolved into distilled water for analysis. Samples of the oxide/salt mixture were analyzed in two ways; two samples were leached with distilled water and two samples were prepared using the nitric acid method described in Section 3.5. The IC and ICPES results are shown in Tables 4.1-1 and 4.1-2 for the fused salt leachate and the dissolved oxide/salt mixture, respectively.

Table 4.1-1 Analytical Results of Fused Salts After Production

Element	Dissolved Fused Salt (mg/L)	Expected* (mg/L)
Cl	26500	28221
Ca	2960	2751
Na	8730	8491
K	11500	11319

*Expected salt composition based on make up (42.5 wt % NaCl, 42.5 wt % KCl, 15 wt % $CaCl_2$) and 1.0156 g of salt dissolved in 20 mL water

Table 4.1-2 Analytical Results of Oxide/Salt Mixtures After Production*

Element	Leachate #1		Leachate #2		Dissolution #1	Dissolution #2	Expected**
	mg/L	µg/g	mg/L	µg/g	µg/g	µg/g	µg/g
Cl	483	9551	467	8873	ND	ND	11100
Na	179	3540	164	3116	2260	5890	3340
K	232	4588	212	4028	3020	6420	4460
Ca	54	1058	47	883	261	4070	1080
Ce	ND	ND	ND	ND	369000	326000	798000

* ND – Not Determined

** Expected concentrations based on 98 wt % CeO_2, 0.85 wt % KCl, 0.85 wt % NaCl and 0.3 wt % $CaCl_2$

The analysis after the humidity test was performed, in part, because a large range of humidity values were measured for test cells that had virtually identical loading conditions. Three samples were taken from the oxide/salt mixture in three test cells. A portion of each sample was used for leaching in 10 mL of distilled water, for dissolving by the sulfuric acid method, and for analysis as a dry sample by NAA. Table 4.1-3 shows the results from IC, ICPES and NAA.

Table 4.1-3 Analytical Results (µg/g) of Oxide/Salt Mixture After Humidity Test

Cell	Ca*	Ce*	Na**	K**	Cl-NAA	Cl-IC***
1-1	1050	712000	3420	4010	8910	4547
1-2	1240	703000	3750	4370	8220	12055
1-3	1090	711000	3470	4190	8310	11844
3-1	1100	715000	3460	4150	8420	11501
3-2	1070	739000	ND	ND	8330	11858
3-3	1210	783000	3420	3880	9810	11898
6-1	1040	696000	3190	3820	8670	11770
6-2	1070	758000	3230	3630	8400	11662
6-3	1140	747000	3410	3940	8100	11535
Expected	1080	798000	3340	4460	11100	11100

* Percent uncertainty – 10%
** Percent uncertainty – 20%
*** Calculated from measurement (mg/L) using total weight of sample

The chemical analyses of the dissolved salts and leached oxide/salt mixtures (Table 4.1-1 and 4.1-2) were in good agreement with expected values based on the make up compositions. The dissolved oxide/salt mixture samples prepared by the nitric acid method showed poor agreement (Table 4.1-2) with expected values (the uncertainty in the data is approximately 10%). The cerium concentration was less than half the expected concentration. These differences are attributed to the sample preparation and probable incomplete dissolution of the oxide. These results lead to the development of the sulfuric acid method for the dissolution of the oxide/salt mixture.

For the oxide/salt samples from the humidity tests, most of the IC chloride measurements were in excellent agreement with the expected value. The NAA chloride concentrations were consistent among the samples but much lower than expected. After receiving this result, an unused quantity of the oxide/salt mixture was analyzed by NAA. The measured chloride concentration was also approximately 8200 µg/g. At this time, no hypothesis exists for this difference. The cations were all measured with ICPES and showed excellent agreement with expected values.

XRD was performed on both the oxide/salt mixture as well as the chloride salt mixture. The oxide/salt mixture was evaluated first and only showed the presence of NaCl and KCl along with CeO_2. Since the chloride salts were a low percentage of the mixture, the fused chloride salts were evaluated to improve the resolution for $CaCl_2$ or other calcium salt that may have formed. The XRD results, as shown in Figure 4.1-1, showed the presence of $KCaCl_3$ and not $CaCl_2$, indicating the complete transformation of $CaCl_2$.

The combined results of the wet chemistry and XRD showed that the oxide/salt mixture is at the target concentration of the desired constituents and that the calcium detected by ICPES is probably present as chlorocalcite, $KCaCl_3$.

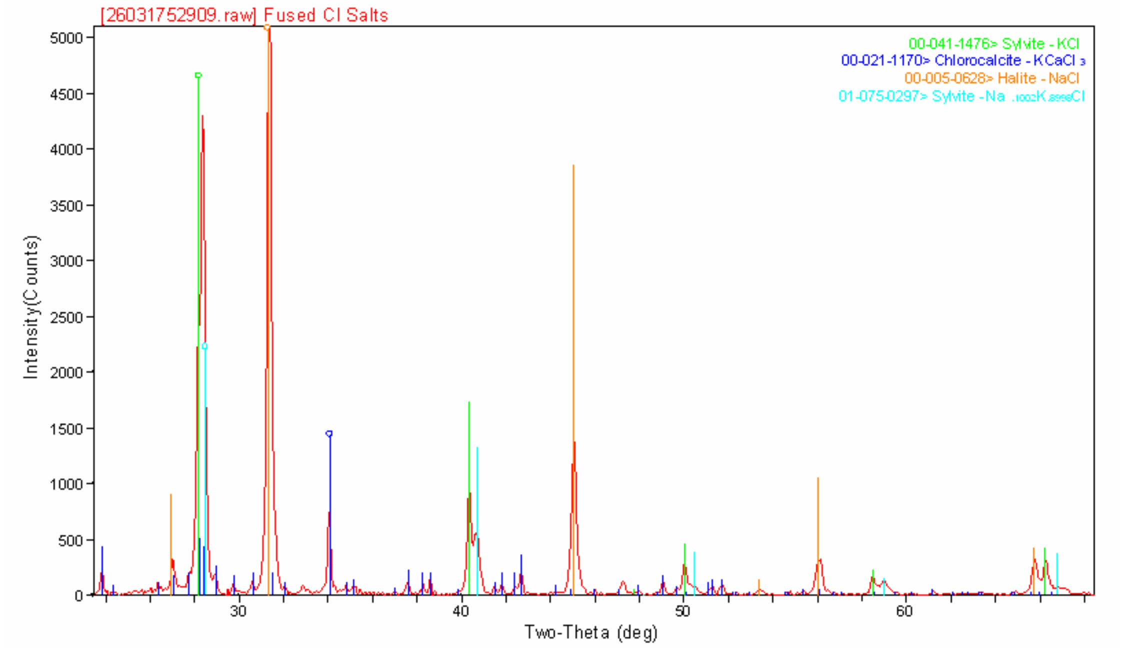

Figure 4.1-1 XRD Results of Fused Chloride Salts (initial salts were NaCl, KCl, and $CaCl_2$).

4.2 WEIGHT CHANGES

The oxide/salt mixture was stored in an inert glove box for a little over a year prior to use. The mixture was contained in a glass jar with a ground conical joint for the top. The glove box humidity levels were typically below 500 ppm. Twenty-gram samples of the mixture, which is equivalent to the quantity used for the humidity tests, were heated to determine if the oxide/salt mixture had picked up moisture during storage. The samples were heated for one hour at 350 °C in an argon-inert furnace. The samples were held in quartz crucibles similar to those used for the initial heating of the salts. The samples lost an average quantity of 0.0188 g of mass (i.e., 0.094 wt %). The range of mass loss was 0.015 to 0.025 g. These weight changes suggest that some moisture was absorbed by the salt mixtures during storage.

The oxide/salt mixture readily picked up moisture when moisture was available. Figure 4.2-1 shows the weight change for a mixture that was loaded sequentially to 0.1, 0.25 and 0.4 wt % water at a relative humidity of 25%. As can be seen in Figure 4.2-1, the rate of moisture pick up decreased as the salts gained water and approached their water saturation point. For low water loadings, the water gain was approximately linear with time. The mixture picked up some moisture during the closing process for the humidity cell and during stabilization in the humidity cell. For this reason, the starting weights for the higher water loadings, such as 0.25 and 0.4 wt % in Figure 4.2-1, were slightly higher than the weights measured at the end of the previous loading step and prior to the closing of the test cell.

The moisture pick up by an oxide/salt mixture was a function of the relative humidity or the amount of water in the gas as well as the time of exposure. The higher the loading relative humidity the shorter the time for loading to a given water content. For a water loading of 0.1 %, the time at 60% RH was approximately 14 minutes whereas at 15% RH the loading time was 62 minutes.

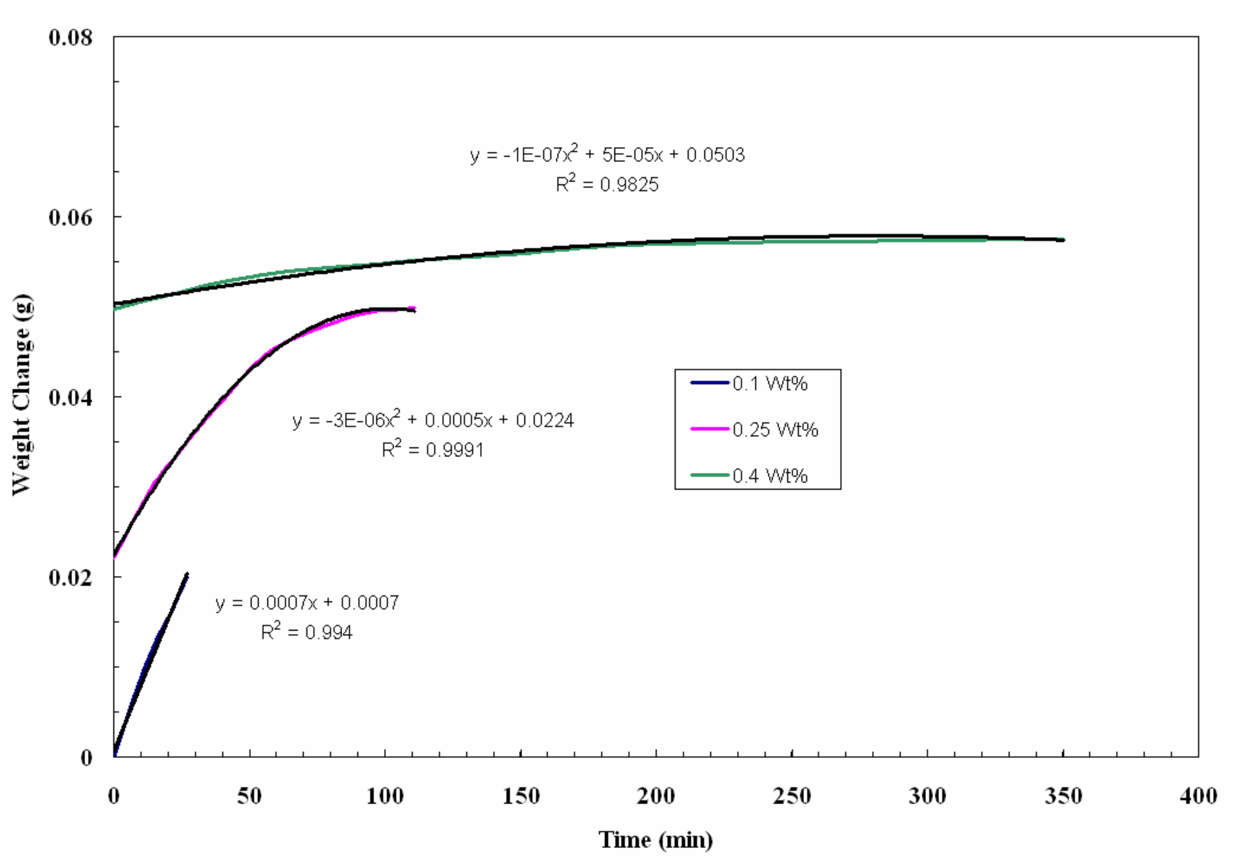

Figure 4.2-1 Weight Change Due to Water Loading of Oxide/Salt Mixture with a Loading Relative Humidity of 25%.

4.3 HUMIDITY CHANGES

Once the desired quantity of water was loaded onto the oxide/salt mixture, the humidity cells were closed and allowed to reach equilibrium. The oxide/salt mixtures, however, picked up additional moisture during the closing process and while reaching equilibrium with the surrounding environment. The amount of moisture pick up depended on the loading relative humidity and the water content of the mixture. The cells remained closed for a variable length of time ranging from 0.5 to 6 days.

Figure 4.3-1 shows the RH change as a function of time for three cells that were loaded to a water content of 0.1 wt % at a loading RH of 40%. One cell had no oxide/salt mixture and was used as a check for the seal of the cell. These humidity responses of the cells were typical for all those observed during this testing. Upon sealing, the humidity cells approached an equilibrium value within approximately 30 minutes.

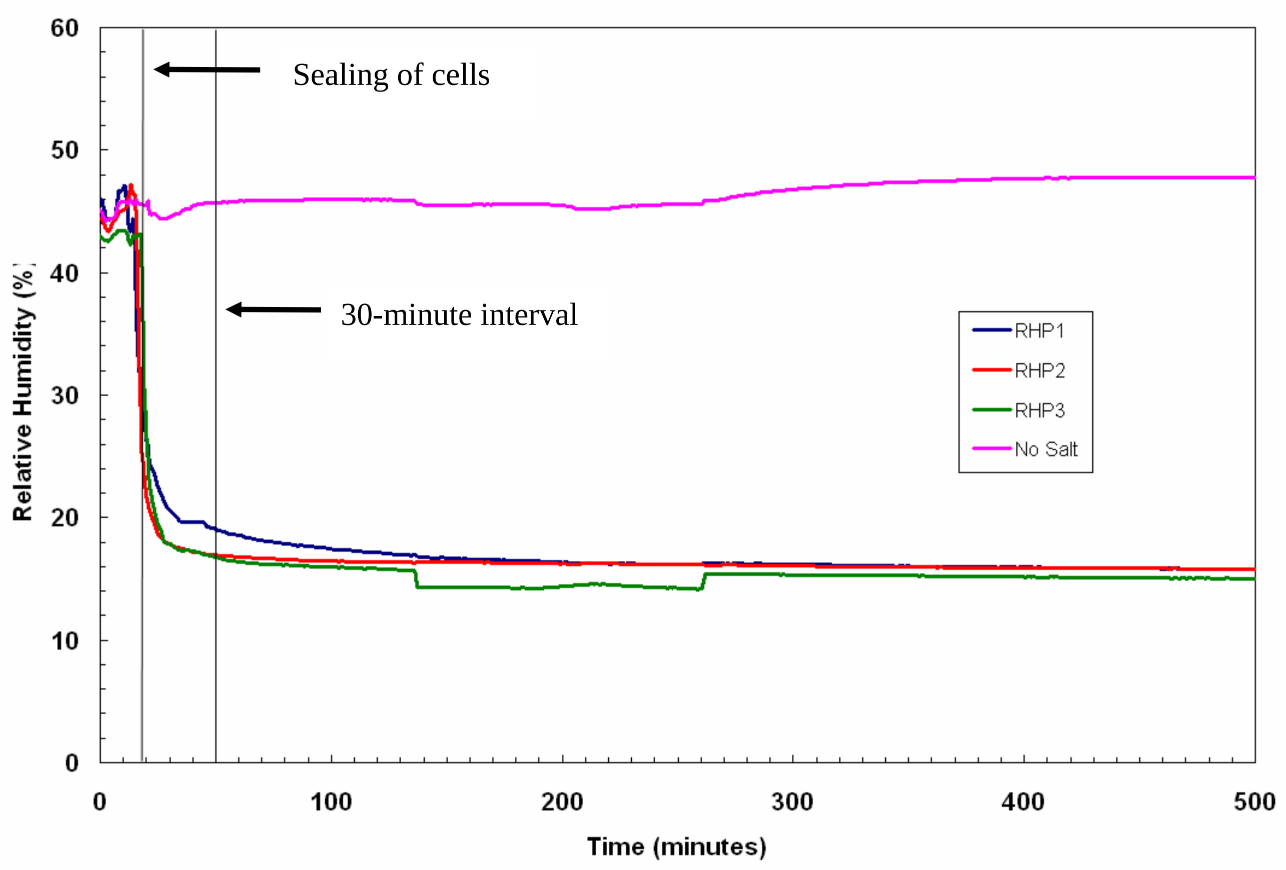

Figure 4.3-1 The humidity change of four cells after closing with 0.1 wt % water at a loading RH of 40 %.

This equilibrium RH was fairly constant but some change was noted by the time the cells were opened. The change in the internal RH between the 30-minute mark and just prior to opening ranged from an increase of 1.7% to a drop of 2.8%. Figure 4.3-2 shows the full RH response for several water loadings at 40% RH in two cells. Transients in the internal RH occurred during storage but were correlated to temperature changes, as shown by the thermocouple (TC2) response for one of the cells. These temperature changes were associated with the operation of the temperature control unit for the laboratory.

The probes were all calibrated, however, there was still a spread in the measured relative humidity for the same experimental condition. This spread can be seen in Figures 4.3-1 and especially in Figure 4.3-2. This difference is more clearly shown by the data in Table 4.3-1. The humidity probe measurements are an average of the ten measurements prior to closing a humidity cell after loading water on to the oxide/salt mixture. The glove bag humidity is also an average of ten points. Measurements were recorded every minute. As can be seen by the data, a difference of up to 5% occurred. The difference between the cell and glove bag humidity probes may be associated with the location in the glove bag as well as response time of the individual probes. The glove bag probe and the cell probes were in separate locations within the bag for ease of working. Many times a single probe would be an outlier from the other probes, although the outlier measurement was not always associated with the same probe. This observation illustrated the importance of having multiple probes associated with a single system.

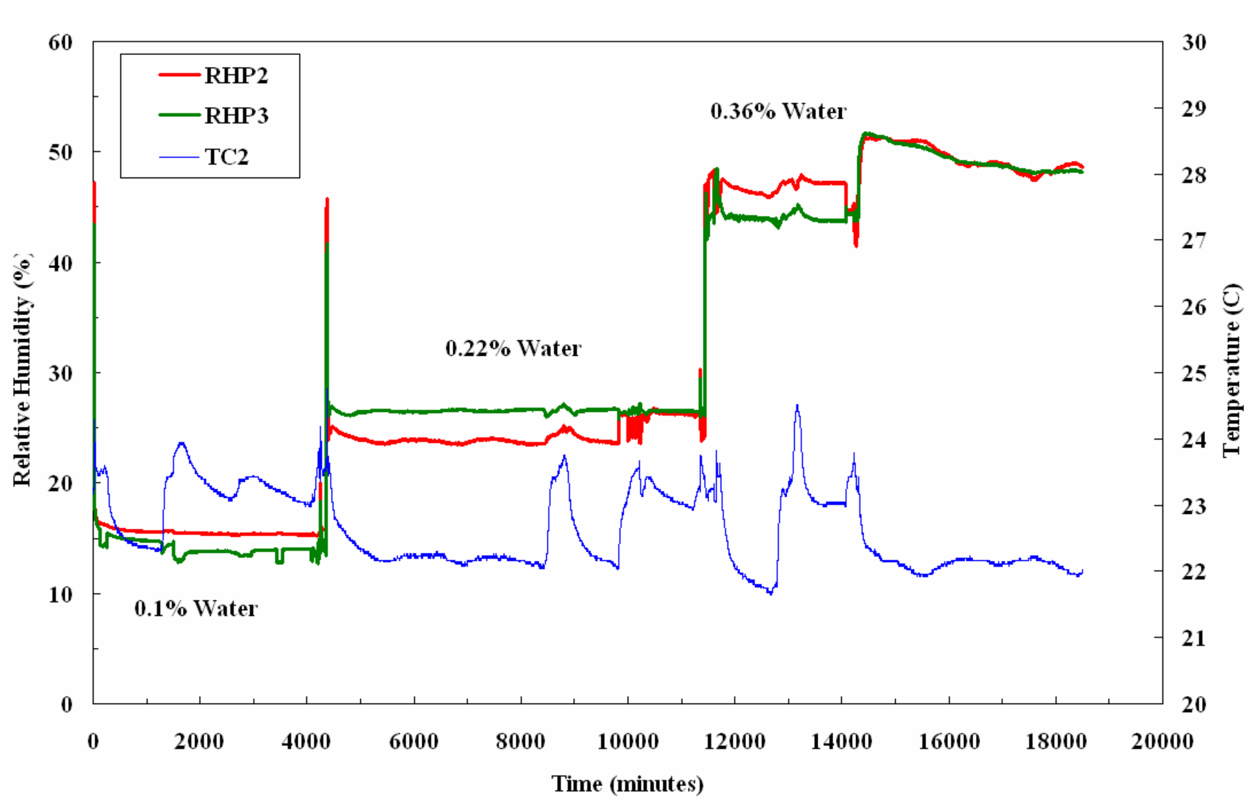

Figure 4.3-2 Internal Relative Humidity Changes of Humidity Cells Loaded to Various Water Loadings at a Loading Relative Humidity of 40%.

The data from each humidity test are summarized in Appendix 1, which lists the loading conditions and the relative humidity and temperature after 30 minutes and at the time the test cell was open. These data are also summarized below in Table 4.3-2, which gives the pertinent humidity values and oxide/salt mixture water content. Several correlations can be observed in these data relative to the equilibrium moisture content of the gas (RH) and the salt/oxide mixture. First, there is a correlation between the equilibrium (30-minute) humidity and the water content on the oxide/salt mixture. This relationship is shown in Figure 4.3-3 with bars indicating the range of values. Also shown in the table is the load time for each condition. As is expected, the longer times are associated with higher water content at lower humidity.

As stated previously, the 30-minute RH varied slightly from the longer time RH measured when the test cell was opened. This variation is related to the water content of the oxide/salt mixture as shown in Figure 4.3-4, which shows a plot of the ratio of the opening RH to that at 30 minutes after closure versus the oxide/salt mixture water content. The ratio approached one at higher water content indicating equilibrium is reached sooner at the higher water content.

Table 4.3-1 Average RH Measurements Prior to Closing Humidity Cells

Glove Bag Probe RH (%)	Test Probe RH* (%)			
	1	2	3	4
49.45	50.23	50.18	48.74	NU
38.91	45.26	45.22	44.85	43.04
39.36	46.88	46.74	46.63	44.38
39.05	47.94	44.33	NU	NU
25.89	33	31.7	30.23	28.07
16.43	15.77	15.42	14.44	NU

* NU – not used

Table 4.3-2 Humidity Data Summary

Water Content (wt %)	**Load Time (min)**	**Relative Humidity (%)**		
		At-Closing	**30-minute**	**At Opening**
0.05	11.5	45.8	16.2	12.6
0.10	62	23.6	17.2	15.7
0.10	26	30.0	17.2	14.4
0.11	16	44.6	17.5	14.9
0.15	14	50.0	18.2	16.5
0.19	227	21.7	20.6	20.7
0.20	68	43.8	24.1	22.1
0.22	32	42.9	26.1	26.4
0.25	128	28.1	27.4	26.4
0.25	46	47.0	28.2	28.2
0.28	345	32.5	31.3	31.1
0.28	10	60.7	33.6	33.2
0.31	33	51.5	36.8	34.7
0.38	232	47.2	45.0	45.4
0.34	258	46.6	45.6	44.8
0.39	22	65.1	47.7	48.9
0.45	92	56.9	50.4	51.2

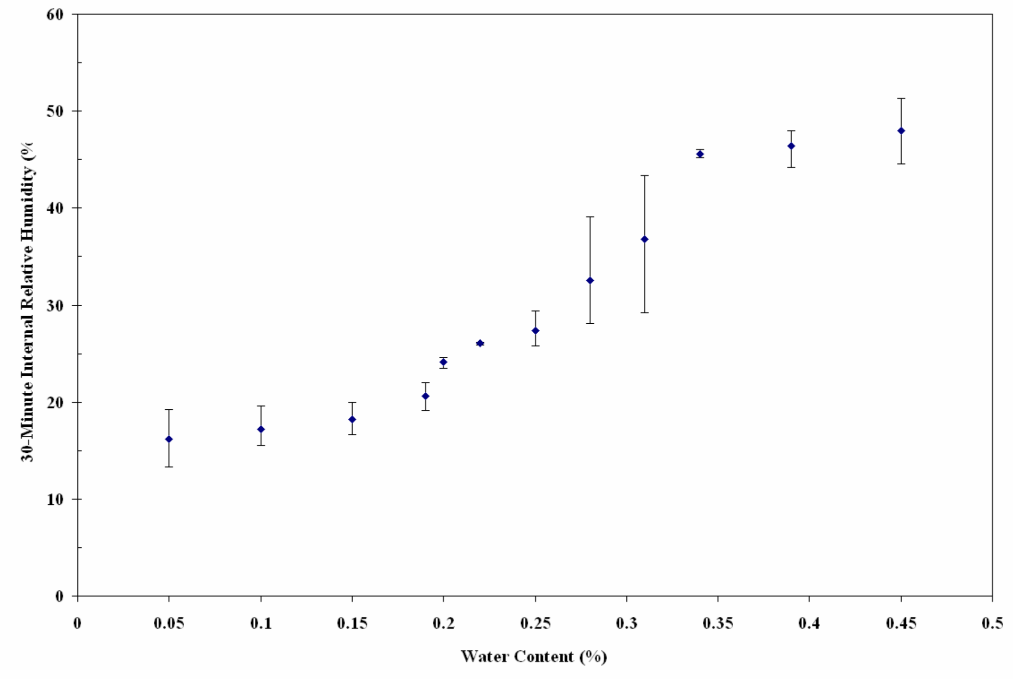

Figure 4.3-3 Relationship of 30-Minute Relative Humidity Values with Oxide/Salt Moisture Water Content.

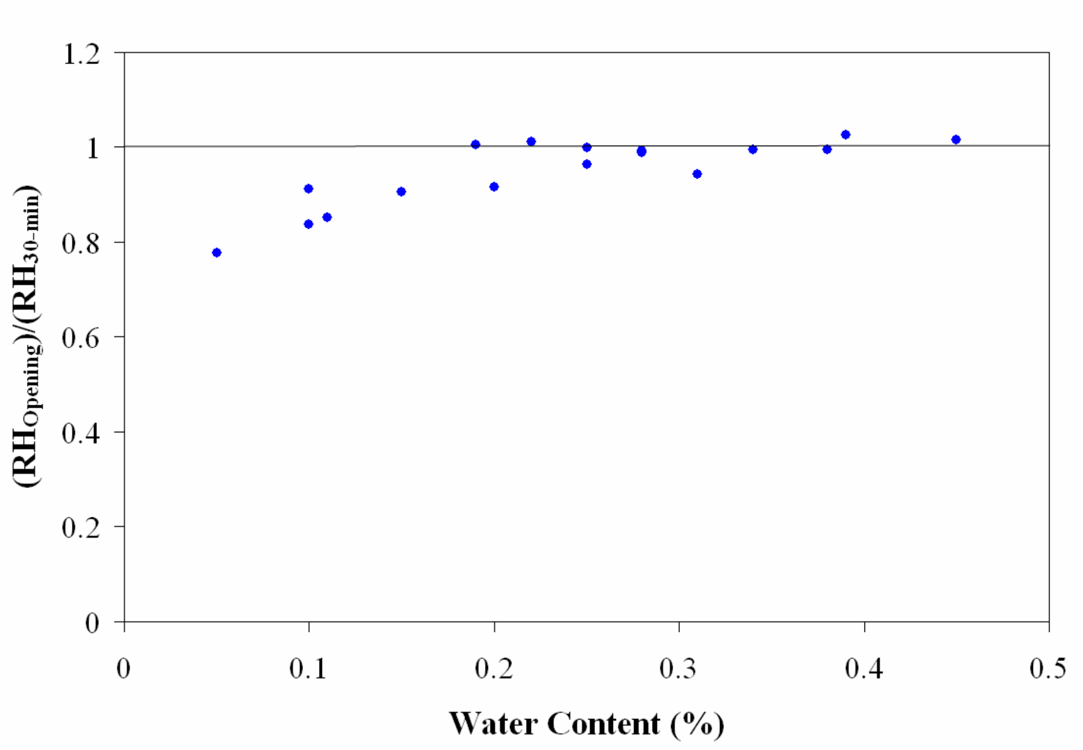

Figure 4.3-4 Relationship of Ratio of Opening RH to 30-minute RH with Oxide/Salt Moisture Water Content.

Another correlation is observed between the ratio of RH at opening and closing to the loading time. As shown in Figure 4.3-5, this ratio approaches one at longer loading times (>100 minutes) indicating that the longer the time to loading the cell the closer the salt/oxide mixture is to an equilibrium water content.

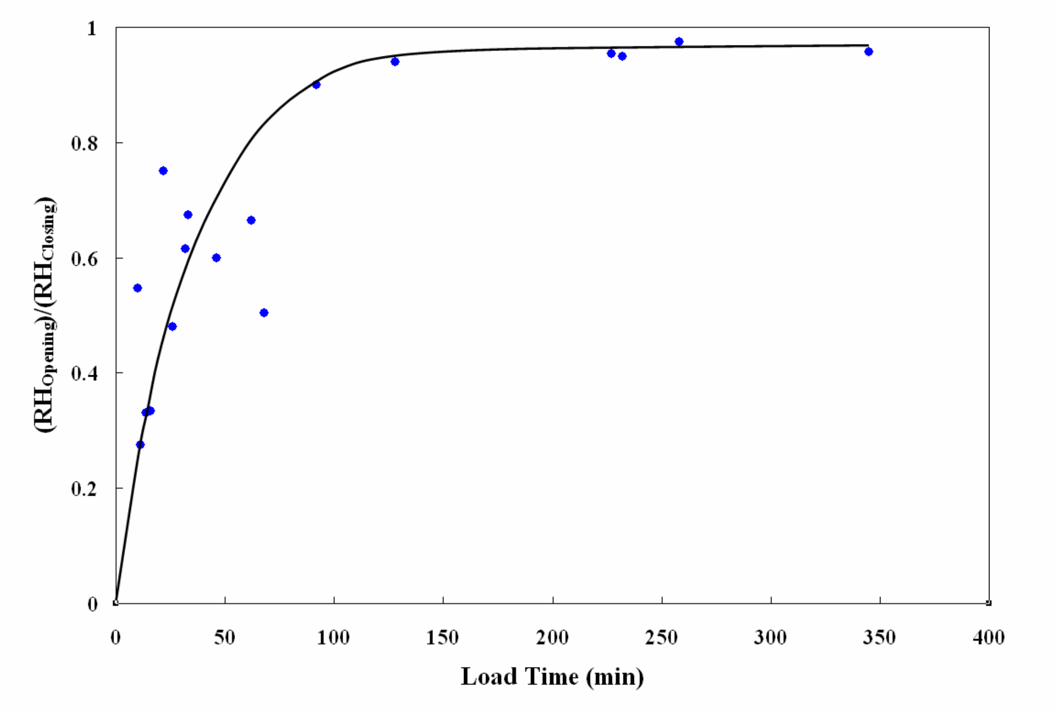

Figure 4.3-5 Relationship of Ratio of Opening Relative Humidity to Closing RH with Loading Time.

Corrosion tests with plutonium-bearing material will be performed at elevated temperatures to simulate actual storage conditions, therefore several experiments with cerium oxide/salt mixtures were performed at elevated temperature to determine the impact of temperature on the relative humidity inside the test cells. Figure 4.3-6 shows the changes in relative humidity, temperature and the dew point for one cell where the temperature was increased from approximately 25 °C to 35 °C and then 50 °C. At approximately 7250 minutes the probes were disconnected from the data acquisition module to move the cells into the oven and then reconnected. In two cases the humidity of the probes shifted as can be seen for probe #1 in Figure 4.3-6. At the end of the 50 °C heating period, the oven was shut off. As can be seen in Figure 4.3-6, as the temperature returned to room temperature, the RH values inside the cells returned to initial values. These data indicate that the good seal for containing the humidity with the cells.

The changes in temperature, dew point and relative humidity for each probe are shown in Table 4.3-3. The values are shown at three times: prior to moving the cells (7200 minutes), at 35 °C (7475 minutes), and at 50 °C (7700 minutes). Two cells (1 and 4) had initial RH near 10% and the other two cells (2 and 3) had initial RH near 20%. The RH and dew point of the cells increased with temperature with each set of cells responding similarly.

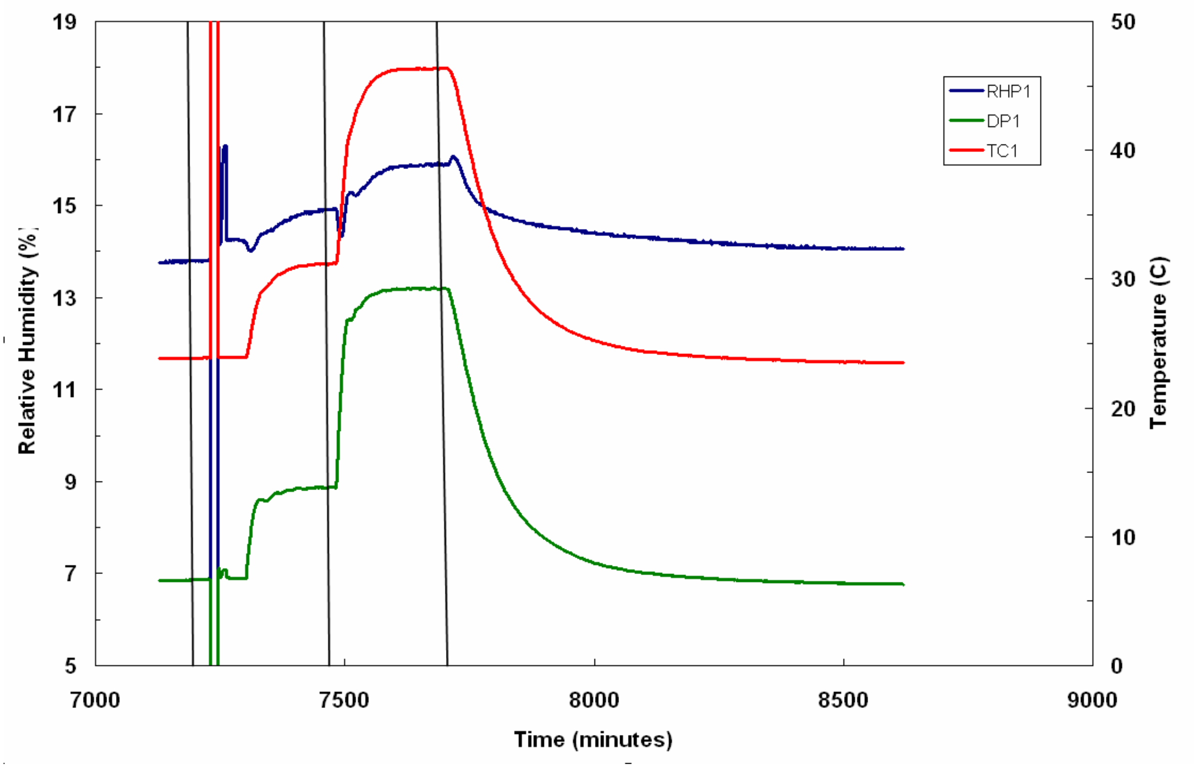

Figure 4.3-6 Humidity and Dew Point Response from Temperature Increases to 35 and 50 °C (vertical lines show measurement points of 7200, 7475, an 7700 minutes).

Table 4.3-3 Relative Humidity and Dew Point Changes as a Function of Temperature For Four Test Cells

Time (min)	**Temperature (°C)**				**Relative Humidity (%)**				**Dew Point (°C)**			
	1	2	3	4	1	2	3	4	1	2	3	4
7200	23.9	24.	24.	24.1	13.8	23.	21.3	11.3	6.7	13.3	13.	5.6
7475	31.2	32.1	31.	31.1	14.9	23.7	21.3	13.2	13.9	21.	19.9	12.9
7700	46.3	47.8	46.	46.6	16.	26.1	22.4	16.7	29.3	37.4	35.6	28.9

5.0 DISCUSSION

The primary goal of the humidity testing was to determine equilibrium RH inside the small-scale corrosion test cell for a given set of conditions (i.e., oxide/salt mixture water content and loading RH) so that the loading conditions for upcoming tests with plutonium oxide containing samples can be determined and the internal RH targeted. These conditions were given in Table 4.3-2 and the results showed that the internal RH is primarily dependent on the water content of the salt/oxide mixture. These results are for the specific composition of the oxide/salt mixture tested and, more specifically, the concentration of chloride salts in that mixture (0.3 wt % $CaCl_2$, 0.85 wt % NaCl, and 0.85 wt % KCl). The loading RH influences the time required to load the water, which is important for setting up the cells in the glovebox. The loading RH also affects the water content on the salt/oxide mixture.

The internal RH is dependent on the water loaded onto the mixture and the composition of the chloride salts. In a system with NaCl, KCl and $CaCl_2$, the NaCl and KCl are not dissolved at a low relative humidity (below the deliquescent point), while all the $CaCl_2$ will dissolve with sufficient water present. For this salt mixture, the XRD results showed that the initial $CaCl_2$ was present as $KCaCl_3$, which deliquesces at 16% relative humidity at 25 °C and readily dissolves in water [4].

For a certain internal RH, the expected water content can be calculated based on EQ3/6, a software package for modeling aqueous systems [5]. Using this software, LANL personnel calculated the expected water content and internal RH relationship for the SRS salt composition [6]. For an internal RH of 45% (aW=0.45) the water content would be 62 g per 0.3 mol of calcium chloride, or 0.56 wt % for the 20 g oxide/salt mixture. In Table 4.3-2, the 45% internal RH was obtained at a measured water content of 0.38 wt %.

Two sources for this difference could be that additional moisture was already present on the oxide/salt mixture or that the salt composition was lower than expected. Based on the analytical results and in particular the calcium concentration, the expected concentration of calcium was present (See Table 4.1-2). After preparation, the salts were stored for approximately one year in an inert glove box and were then used without further processing. When the above discrepancy was found, 20-g samples of the stored oxide/salt mixture were heated to 350 °C for one hour to drive off any moisture. The samples lost an average mass of 0.0188 g. The total water content for these mixtures, therefore, would be about 0.09 wt % greater than reported. At 45% RH, the new water content would be 0.47 %. Based on the range of the mass differences (0.015 to 0.025 g), the water content would range from 0.455 % to 0.505 %.

During the humidity testing, the measurement of the RH had a spread of up to 5% RH among the different probes, which could be associated in part with probes having different response times. The use of an average value would then not represent the actual RH. A small error of 1% RH would shift the expected water content. For example in Table 4.3-2 the average internal RH of 45% at 30 minutes was from actual measurements of 44.2% and 45.7% (See Appendix 1). The expected water content then would range between 60 and 63.5 g or 0.54 wt % to 0.572 wt %.

6.0 CONCLUSIONS

To support the small-scale experiments using plutonium oxide/salt mixtures, a non-radioactive series of experiments was conducted to determine the initial relative humidity condition of the small-scale test cell once it was closed at a given loading relative humidity and an oxide/salt-mixture water content. The non-radioactive humidity tests have established some guideline conditions for loading the small scale test cell. The testing showed that a range of initial RH (16-50%) could be obtained depending on the loading relative humidity (18-60%) and oxide/salt mixture water content (0.05-0.45 wt %). Within the known errors for the non-radioactive humidity test, the results showed that the humidity may be estimated by calculations using software EQ3/6.

7.0 ACKNOWLEDGEMENTS

The authors would like to acknowledge the talented assistance of Vickie Timmerman in conducting the experimental work and Dr. Mac Louthan, Jr. for helpful discussions. The discussions with Dr. Kirk Veirs and assistance from Dr. Michael Martinez-Rodriquez were important for interpretation of the data.

8.0 REFERENCES

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APPENDIX 1: Humidity Test Data

	Loading Conditions			At Closing		30-Minute		At Opening		
Probe #	Humidity (%)	Water (%)	Time (min)	Humidity (%)	TC (C)	Humidity (%)	TC (C)	Humidity (%)	TC (C)	Time (min)
1	18.6	0.10	56	24.5	22.6	17.9	22.9	15.9	22.8	1396
2		0.10	67	22.6	22.7	16.5	22.8	15.5	22.7	1396
Avg		0.10	62	23.6		17.2		15.7		
Std Dev		0.00	7.78	1.34	0.07	0.99	0.07	0.28	0.07	
1	17.7	0.19	227	22.7	22.4	22.0	22.7	22.0	23.7	7337
2		0.18	226	20.6	22.4	19.1	22.6	19.3	23.7	7337
Avg		0.19	227	21.7		20.6		20.7		
Std Dev		0.01	0.71	1.48	0.00	2.05	0.07	1.91	0.00	
1	25-26	0.10	27	32.2	23.7	19.6	23.1	15.3	22.2	2800
2		0.10	25	30.0	23.6	16.6	23.2	15.3	22.2	2790
3		0.10	25	27.8	24.0	15.5	23.4	12.7	22.1	2789
Avg		0.10	26	30.0		17.2		14.4		
Std Dev		0.00	1.15	2.20	0.21	2.12	0.15	1.50	0.06	
1	25-26	0.25	111	30.8	23.9	29.4	23.3	29.2	23	6719
2		0.25	139	27.8	23.9	27.0	23.5	25.9	23.2	6689
3		0.25	134	25.6	23.9	25.8	23.6	24.2	23.3	6697
Avg		0.25	128	28.1		27.4		26.4		
Std Dev		0.00	14.93	2.61	0.00	1.83	0.15	2.54	0.15	
1	25.5- 28.5	0.29	350	33.6	22.9	34.1	22.5	34.1	22.9	2325
2		0.28	350	33.0	23.0	31.6	22.8	31.4	22.9	2333
3		0.28	334	31.0	22.5	28.2	22.9	27.8	22.9	2332
Avg		0.28	345	32.5		31.3		31.1		
Std Dev		0.01	9.24	1.36	0.26	2.96	0.21	3.16	0.00	
3	40.3	0.25	45	45.0	22.8	28.1	23.3	27.9	23.8	8825
4		0.25	46	48.9	22.8	28.2	23.4	28.5	24	8822
Avg		0.25	46	47.0		28.2		28.2		
Std Dev		0.00	0.71	2.76	0.00	0.07	0.07	0.42	0.14	
3	40.4	0.37	252	45.6	23.2	44.2	23.4	44.6	24	8380
4		0.39	211	48.7	23.1	45.7	23.6	44.9	24	8423
Avg		0.38	232	47.2		45.0		44.8		
Std Dev		0.01	28.99	2.19	0.07	1.06	0.14	0.21	0.00	
1	38.8	0.10	14	44.9	23.5	19.0	23.5	15.6	22.9	4050
2		0.11	16	45.8	23.2	16.9	23.6	15.3	23	4050
3		0.12	17	43.0	23.4	16.7	23.7	13.8	23	4050
Avg		0.11	16	44.6		17.5		14.9		
Std Dev		0.01	1.53	1.43	0.15	1.27	0.10	0.96	0.06	
1	39.8	spilled	49	45.5	23.3	37.2	23.6	38.0	22.8	6950
2		0.22	23	44.4	23.6	25.9	23.5	26.2	23.3	6978
3		0.22	23	41.4	24.2	26.2	23.6	26.5	22.8	6971
Avg		0.22	32	42.9		26.1		26.4		
Std Dev		0.00	0.00	2.12	0.42	0.21	0.07	0.21	0.35	
1	41.4	0.29	276	47.6	23.2	46.1	23.4	46.9	23.3	2500

2		0.37	217	46.6	23.1	45.4	23.4	44.9	23.6	2500
3		0.36	281	45.5	23.4	45.2	23.6	44.4	23.4	2500
Avg		0.34	258	46.6		45.6		45.4		
Std Dev		0.04	35.59	1.05	0.15	0.47	0.12	1.32	0.15	
4	39.2	0.05	10	45.6	25.6	13.25	25.5	11.3	24.1	7022
1	37.9	0.05	13	45.9	25**	19.2	25.4	13.8	23.8	7002
Avg		0.05	11.50	45.8		16.2		12.6		
Std Dev		0.00	2.12	0.21	0.42	4.21	0.07	1.77	0.21	
2	38.1	0.20	65	44.9	25.1	24.6	25.7	22.8	24	6966
3	38.2	0.20	70	42.6	25.4	23.5	25.7	21.4	24	6945
Avg		0.20	68	43.8		24.1		22.1		
Std Dev		0.00	3.54	1.63	0.21	0.78	0.00	0.99	0.00	
2	49.9	0.13	12	48.7	25.6	16.6	25.7	15.4	23.6	8612
3		0.14	12	50.4	25.5	18.0	25.4	13.9	23.5	8609
4		0.18	19	50.8	25.8	20.0	25.5	20.3	23.5	8605
Avg		0.15	14	50.0		18.2		16.5		
		0.03	4.04	1.12	0.15	1.71	0.15	3.35	0.06	
2	46.6	0.29	25	49.3	25.4	29.2	25.0	28.5	22.8	2580
3		0.30	32	51.2	24.7	37.9	23.9	35.0	23.1	2572
4		0.34	43	54.0	24.8	43.4	23.0	40.7	23	2561
Avg		0.31	33	51.5		36.8		34.7		
		0.02	9.07	2.36	0.38	7.16	1.00	6.10	0.15	
2	52.5	0.45	45	57.6	23.7	44.6	24.2	45.4	21.5	3986
3		0.46	94	54.8	25.0	51.3	24.6	52.6	21.6	3922
4		spilled	137	58.3	24.3	55.4	23.8	55.5	21.6	3885
Avg		0.45	92	56.9		50.4		51.2		
		0.00	34.65	1.98	0.92	4.74	0.28	5.09	0.07	
1	60.4	0.30	12	59.0	23.8	39.1	23.9	39.3	23.2	4000
2		0.25	7	62.3	23.4	28.1	23.8	27.1	23.1	4000
Avg		0.28	10	60.7		33.6		33.2		
Std Dev		0.04	3.54	2.33	0.28	7.78	0.07	8.63	0.07	
1	61.4	0.40	19	63.5	23.9	47.4	24.4	47.4	24.2	4200
2		0.38	24	66.6	23.7	48.0	23.8	50.4	24	4200
Avg		0.39	22	65.1		47.7		48.9		
Std Dev		0.02	3.54	2.19	0.14	0.42	0.42	2.12	0.14	