LA-UR- 0 2- 5 1 0 3

Title: Water sorption mechanisms for MIS materials

Author(s): D. Kirk Veirs, 093385, NMT-11
Richard E. Mason, 096081, NMT-11
Randall M. Erickson, 091271, NMT-DO

Los Alamos
NATIONAL LABORATORY

Water sorption mechanisms for MIS materials

D. Kirk Veirs, Richard Mason, and Randall Erickson
Nuclear Materials Technology Division
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

ABSTRACT

The fundamental processes that control the amount of water sorbed by impure plutonium-containing materials after calcination are reviewed. Of particular interest is the amount of and rate of moisture sorption at 1000 PPM_V (parts-per-million vapor; ~3% RH at 25 °C) and 10,000 PPM_V (32% RH at 25 °C). Pure plutonium oxide powders will remain below the 0.5 wt% criterion for packaging in the DOE 3013 Standard at both water vapor concentrations [1]. Deliquescent salts that have been observed in calcined materials by DOE's Materials Identification and Surveillance (MIS) program will exceed the 0.5 wt% criterion at 10,000 PPM_V and will meet that standard at 1,000 PPM_V. Hydrated salts will exceed the 0.5 wt% criterion at all technologically achievable water vapor concentrations if allowed to reach equilibrium. Controlling the moisture availability by controlling the atmospheric content at 1000 PPM_V and limiting the access to atmospheric moisture after stabilization through the use of a properly configured stabilization boat will minimize moisture uptake by these materials.

INTRODUCTION

Plutonium oxide materials take up water from the atmosphere. The extent of water uptake is dependent upon the temperature, relative humidity, composition, and specific surface area (SSA). The DOE 3013 Standard specifies that materials packaged for long-term storage must not exceed 0.5 wt% of water (The DOE 3013 Standard uses the term moisture content to refer to any chemical that might produce water such as hydrates and hydroxides [1]). Controlling the water vapor content of the atmosphere to which materials will be exposed prior to packaging is one approach to ensuring that the 0.5-wt% criteria will be met. In a processing environment, there is a trade-off between dollars and the water vapor content of the atmosphere. Although it is possible to lower the water vapor content of the processing atmosphere to arbitrarily small amounts, the cost to do so rises substantially as the water vapor content decreases. At some point, the benefit from lowering the water vapor content of the processing environment is not incrementally increased. This benefit break-even point varies with the composition of the material and how the material is handled between calcination and welding of the final package.

The chemical composition of impure plutonium oxide materials destined for long-term storage is not specified in the DOE 3013 Standard other than to require that the material must be greater than 30% plutonium oxide. The MIS program has identified a short list of materials that will be found in impure plutonium oxide materials prior to stabilization. In addition to plutonium oxide itself, there are halide salts and oxides of magnesium and calcium and halide salts of sodium and potassium [MgO, $Mg(OH)_2$, CaO, $Ca(OH)_2$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, KCl, $NaCl$ and numerous variations of these] [2,3].

The water uptake by these materials and their stabilized products in atmospheres of various water contents will be considered in order to provide guidance on the optimum water vapor content of processing glove boxes. A thermodynamic approach will be used in most instances. In the final analysis, limiting the moisture content below 0.5 wt% for materials containing hydrated salts will require the limitations imposed by material balance, diffusion, and ultimately the kinetics of moisture uptake.

We will now discuss the potential moisture content of the three classes of materials: pure plutonium oxide, deliquescent salts, and hydrated salts.

PLUTONIUM OXIDE POWDER

For most materials to be packaged, plutonium dioxide is the most abundant compound to be considered and the most important in regards to its ability to generate hydrogen gas from water. Plutonium oxide is thought to interact with water in much the same way as most metal oxides. [4,5] The clean plutonium oxide surface will be terminated with oxygen atoms, not plutonium atoms. Typical oxygen terminated oxide surfaces are slightly hydrophobic and impinging water molecules do not readily stick to the clean surface. Well-annealed surfaces with few defect sites tend to react slowly with water.[5,6] However, those water molecules that stick to defect sites react to form terminating hydroxyl species. The hydroxyl-terminated surface grows and is now hydrophilic due to its capability for hydrogen bonding with water. A second layer formed of molecular water has a heat of adsorption of approximately 84 kJ mol^{-1}, about 40 kJ mol^{-1} higher than the heat of vaporization of water.[5] This heat of adsorption is consistent with adsorbed water hydrogen bonding to two surface hydroxyls.[6] Additional water, up to about 8 monolayer-equivalents, appears to have a heat of adsorption about 7 kJ mol^{-1} above the heat of vaporization of water.[7,8,9,10] Water adsorbed in addition to these layers behaves like liquid water with respect to vapor pressure.[10] Water adsorbs onto plutonium oxide surfaces with a surface density of typically 0.22 mg m^{-2}.[7,10] Therefore, the amount of water in the first hydroxyl layer is 0.11 mg m^{-2}, and the amount of water in any additional layer is 0.22 mg m^{-2}.

The specific surface area (SSA) of plutonium oxide powder can vary from 100 m^2 g^{-1} to less than 0.1 m^2 g^{-1}. Calcination of high-surface area powders results in large reductions in the SSA. The highest measured SSA of plutonium oxide powders after calcination to 950 °C by the MIS program is less than 5 m^2 g^{-1}.[3,4] Therefore, if there is no measured SSA for a material to be packaged either before or after calcination, then a conservative number of 5 m^2 g^{-1} can be assumed. Using 5 m^2 g^{-1} SSA, the hydroxyl layer in 5 kg of plutonium oxide powder represents 2.8 g of water and the second, strongly adsorbed layer represents 5.5 g of water. Three additional layers of water are required for the water content of the oxide to approach the 0.5 wt.% criterion.

Plutonium oxide powder that is in equilibrium with atmospheric moisture will include the surface hydroxyl layer and a second, strongly adsorbed molecular water layer even at extremely low relative humidity. Additional layers of water will sorb depending upon the relative humidity of the air. Calcination of this material will result in loss of water depending upon the calcination temperature. Calcination to 600 °C will remove all molecular adsorbed water including the strongly bound second layer. Removal of the hydroxyl layer is generally thought to occur by 950 °C.[5] The resulting clean oxide surface will react with moisture in the atmosphere to reform the hydroxyl layer.[7,8,9,11,12] The kinetics of this reaction have been measured in 1% RH air to be 1.8 x 10^{-4} g water m^{-2} h^{-1}, which would result in a complete hydroxyl layer in less than 1.5 hours. Assuming the rate to be the same to add the second, strongly bound molecular water layer, in three hours after calcining, these two layers will be formed even in low RH atmospheres. Formation of these two layers in atmospheres with very low partial pressures of water is also consistent with the experimentally measured heats of adsorption for these layers and with XPS measurements on well-characterized materials.(Schulze, Farr et al. 2000)
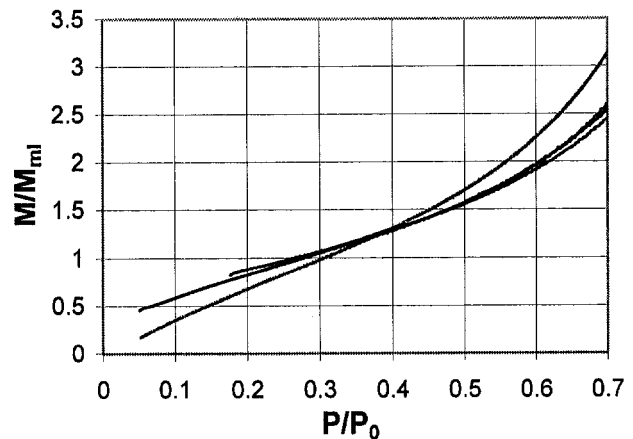

Figure 1. Adsorption isotherm of water onto plutonium oxide powder calcined to 200 °C. The three experimental curves are for 25 and 50 grams of plutonium oxide exposed to 100 µl of water and 25 grams exposed to 25 µl of water. The grey curve is calculated using BET theory with a heat of adsorption for water onto the powder of -5.4 kJ mol^{-}

The y-axis is the mass of sorbed water normalized to the mass of a sorbed monolayer of water. The x-axis is the observed water vapor pressure divided by the saturated water vapor pressure and corresponds to the relative humidity (RH).

The adsorption of water onto plutonium oxide powders containing the hydroxyl layer and the second layer has been studied.[10] The adsorption isotherm shows that the amount of adsorbed water is a well-behaved function of the RH. Figure 1 shows that a RH of 60% or higher is required to add three additional monolayers, which would exceed the 0.5 wt. % criterion assuming 5 m^2 g^{-1} SSA or higher.

EXPECTED SALT IMPURITIES

The plutonium processes that generated the material destined for long-term storage under DOE's 3013 Standard used salt mixtures containing NaCl, KCl, $MgCl_2$ and $CaCl_2$. Materials containing $MgCl_2$ and $CaCl_2$ will pick up moisture from the glove box atmosphere resulting in $MgCl_2 \cdot xH_2O$ and $CaCl_2 \cdot xH_2O$, where x can be from 1 to 6. The 3013 Stabilization process requires the material to be calcined to 950 °C for two hours. Calcination of these salts results in (1) loss of material due to evaporation, (2) loss of water, (3) hydrolysis of the $MgCl_2$ to MgO, (4) potentially hydrolysis of some of the $CaCl_2$ to CaO, and (5) potentially the formation of ternary salts such as $KMgCl_3$ (carnallite), Mg_2CaCl_6 (tachyhydrite), $KCaCl_3$, and Na_2MgCl_4. MIS materials have been characterized by elemental analytical chemistry and x-ray diffraction both before and after calcination. [2] Species identified in XRD include PuO_2, NaCl, KCl, hydrated $CaCl_2$ (sample had been exposed to air prior to analysis), and MgO. A number of unidentified XRD peaks were also observed. No XRD peaks due to $MgCl_2$ were observed. Elemental analysis of the calcined material can be used to develop an anion and cation material balance. In some cases there is not enough chlorine to balance the cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}), suggesting that some of the cations exist as oxides, such as MgO. In some cases there is a balance of cations and anions. Since no MgCl2 is observed in these samples by XRD, this suggests that the formation of ternary

salts may have occurred as there were unidentified XRD peaks.

Calcination of $CaCl_2 \cdot 6H_2O$ results in loss of the six waters of hydration by 200 °C and the remaining $CaCl_2$ melts at 775 °C. [16] The $CaCl_2$ should sublime and the calcined materials should have no Ca salts if equilibrium was reached. CaO is formed at temperatures above 450 °C by the hydrolysis of $CaCl_2$ by water with the release of HCl. [17] Gas phase water above 450 °C is observed in TGA analysis of MIS materials. [18]

Calcination of $MgCl_2 \cdot 6H_2O$ is more complicated. $MgCl_2 \cdot 6H_2O$ loses four waters of hydration by 200 °C, and then decomposes by hydrolysis releasing HCl at higher temperatures. The resulting material after calcination at 950 °C should be MgO if the hydrolysis reaction is driven to completion. However, the MIS characterization sees residual magnesium and chloride in calcined impure oxides in amounts that suggest not all $MgCl_2 \cdot 6H_2O$ has hydrolyzed to MgO [3,4]. $MgCl_2$ in the presence of $CaCl_2$, NaCl and KCl also form ternary salts at high temperatures such as Mg_2CaCl_6, $KMgCl_3$, and Na_2MgCl_4. [19,20,21]

The expected salt impurities will be predominately NaCl, KCl, and $CaCl_2$. Magnesium containing salts that might exist are Mg_2CaCl_6, $KMgCl_3$, and Na_2MgCl_4. Calcium and magnesium will also exist as oxides that behave similar to plutonium oxide with respect to moisture sorption.

DELIQUESCENT SALTS

Deliquescent salts for the purpose of this discussion are the chloride salts that do not incorporate waters into their crystal lattice such as NaCl and KCl. Based on process knowledge and confirmed by MIS, these are the only significant simple chlorides expected to be sealed in 3013 containers. Hydrated salts such as $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ also deliquesce, however, these types of materials will contain sufficient water to exceed the 0.5wt% criterion before they deliquesce.

The water adsorption behavior of deliquescent materials is relatively easy to understand and threshold values of RH that ensure the 0.5 wt%

criterion is met can be assigned based on literature data. Simple salts form a single monolayer of water on their surface when exposed to water vapor at a RH below their deliquescent RH. The surface begins to dissolve at the deliquescent RH and the salt continues to take-up water until the entire crystal is dissolved. The deliquescent points for NaCl and KCl are 75% and 84% RH respectively. The SSA of these materials following calcination at temperatures exceeding the melting point is generally quite small, therefore, these materials adsorb very little water until the relative humidity of their deliquescent point is reached. Compounds formed from mixtures of simple salts are described by colligative properties in which the deliquescent point is reduced depending upon the mole fractions of each material. The maximum reduction in the deliquescent point can be used as the threshold RH that ensures less than 0.5 wt% water adsorption. For an equimolar mixture of KCl and NaCl, the deliquescent point is reported to be 72% RH.(Tang and Munkelwitz 1994)

Calcination of simple salts removes any water adsorbed in the surface monolayer. The salts melt at temperatures below the 3013 specified calcination temperature of 950 °C, e.g. NaCl 800 °C and KCl 771 °C. Melting of the salts will result in a very low SSA material for packaging. In addition to melting, some of the salt will evaporate or sublime during calcination as shown by MIS results. Under equilibrium conditions, all of the salt would have evaporated or sublimed leaving pure plutonium oxide powder for packaging. However, the length of time for calcination and the kinetics of evaporation leave behind much of the salt for packaging. The maximum amount of Na or K after calcination observed by the MIS program is 3.0 wt%.[3,4]

Table II: Deliquescent points of some inorganic compounds at 25°C. [14,15]

Compound	RH	Compound	RH
LiCl·H$_2$O	11%	KI	69%
CaBr$_2$·6H$_2$O	16%	NaNO$_3$	74%
LiI·3H$_2$O	18%	NaCl	75%
CaCl$_2$·6H$_2$O	29%	KBr	81%
KF	31%	(NH$_4$)$_2$SO$_4$	81%
MgCl$_2$·6H$_2$O	33%	KCl	84%
Ca(NO$_3$)$_2$·4H$_2$O	51%	CsI	91%
Mg(NO$_3$)$_2$·6H$_2$O	53%	KNO$_3$	92%
NaBr·2H$_2$O	58%	K$_2$SO4	97%

The RH of the deliquescent point for the salts expected to be packaged under the 3013 standard are higher than 29%. Therefore, maintaining a glove box atmosphere RH of less than 29% will ensure that these materials will not sorb sufficient water to exceed the 0.5wt% criterion. The RH of a 10,000 PPM$_V$ atmosphere at 25 °C is slightly greater 29% and material stored for short periods of time between calcining and packaging may sorb sufficient moisture to exceed the 0.5wt% criterion. The RH of a 1,000 PPM$_V$ atmosphere at 25 °C is sufficiently below the deliquescent point for salts expected to be in materials to be packaged that minor amounts of water will be sorbed as a surface monolayer.

HYDRATED SALTS

Chloride salts of magnesium and calcium and many of the expected ternary compounds are examples of salts with waters incorporated into their crystal lattice, e.g. MgCl$_2$·6H$_2$O, CaCl$_2$·6H$_2$O, Mg$_2$CaCl$_6$·12H$_2$O (tachyhydrite), and KMgCl$_3$·6H$_2$O (carnallite). Based on process knowledge, as confirmed by MIS elemental characterization, these appear to be the only hydrated chlorides of consequence that need to be evaluated with respect to sealing into 3013 containers. The behaviors of these materials with water are relatively complex and they are the most difficult to establish a threshold criterion for RH to ensure that less than 0.5 wt% water will be sorbed between calcination and packaging. Many hydrated chlorides deliquesce in the same manner as simple salts. In general, their deliquescent RH is lower than for simple salts, e.g., 33% for MgCl$_2$·6H$_2$O and 29% for CaCl$_2$·6H$_2$O. Hydrated salts also will exhibit colligative behavior and a lower deliquescent RH is expected for mixtures. However, their deliquescent RH is not really the primary issue with these salts, because the amount of water in the pure compound can easily exceed the 0.5 wt% bulk criterion when even small amounts of the hydrates are present, e.g. 47 g of MgCl$_2$·6H$_2$O and 51 g CaCl$_2$·6H$_2$O respectively in 5 kg of material.

Calcium and magnesium oxides formed by calcination will react with water to form surface hydroxide species. [22,23,24,25,26,27,28] These will adsorb water in a manner similar to the

hydroxylated plutonium oxide surface. The SSA of these materials after calcination is probably well below 1 $m^2 g^{-1}$ and the amount of water adsorbed will be small. Residual $CaCl_2$ and $MgCl_2$ will react with water to reform hydrated salts. The strength of the interaction of the waters of hydration and the salt will vary depending upon the degree of hydration. Equilibrium between the various hydrated species and the partial pressure of water in the gas phase will be formed. The stability of the various hydrates is strongly dependent upon temperature. The temperature range of stability for the hydrates of $CaCl_2$ are given in Table III.

Table III. Temperature range of stability for the hydrates of calcium chloride. [29]

Compound	Lower T	Upper T
CaCl2	230 °C	Melts at 772 °C
CaCl2•(1/3)H2O	187 °C	230 °C
CaCl2•H2O	176 °C	187 °C
CaCl2•2H2O	46 °C	176 °C
CaCl2•4H2O	30 °C	46 °C
CaCl2•6H2O	-	30 °C

TGA curves of $MgCl_2 \cdot 6H_2O$ show that the loss of the first water of hydration occurs around 100 °C.[30, 31] At room temperature, reducing the RH to a level where hydration of $CaCl_2$ and $MgCl_2$ salts will not form is not practical. In addition, $CaCl_2$ will begin picking up moisture during cooldown after calcinations at 230 °C, extending the time during which moisture sorption can occur compared to those materials that physically adsorb moisture onto their surface. Any $MgCl_2$ that is present will start to sorb moisture at higher temperatures.

The range of stability of the hydrated ternary salts and their water sorption behavior is not well known. However, their behavior should not be much different than calcium and magnesium chloride. Therefore, in the case of impure materials containing calcium and magnesium, the ability to keep the water content below 0.5 wt% will depend upon the kinetics of absorption and mass transfer rather than thermodynamics.

KINETICS

The kinetic processes that affect water sorption by materials are highly geometry dependent. Therefore, this discussion will be generic in nature.

The important processes are the fundamental kinetic rates of water sorption by materials, diffusion of the atmospheric species to the materials and into the materials, and convective processes such as occurs in furnaces and glove boxes with ventilation systems. The reported fundamental time constants for moisture sorption onto Mg and Ca oxides are between 10 and 30 minutes (1/e point in the sorption curve). [32] These time scales are rapid compared to the time between calcination and packaging. Limiting the availability of water vapor and diffusion processes must be considered.

The properties of water at 24 °C are given in Table IV. A typical glove box of six cubic meters at 5,700 PPM_V contains 25 g of water in the atmosphere, enough to produce 0.5 wt% mass gain if totally absorbed. In a glove box with a static atmosphere at 1000 PPM_V there is not enough water to reach 0.5 wt% water adsorbed and the adsorption of the atmospheric water by the material in the glove box will lower the water content in the glove box atmosphere to a very low equilibrium value. In a glove box with atmospheric make-up such as is commonly used at RFETS or Hanford, the make-up supply continuously adds water to the system, which will allow material kept in these glove boxes to continuously sorb water. In a glove box containing calcination furnaces, water will be added to the glove box atmosphere by the calcining of material and will be removed by the glove box ventilation system when the water content is above that of the make-up supply. Calcining material with substantial amounts of water can raise the relative humidity within the glove box to levels where most materials will readily sorb water. The efficiency of water removal by the ventilation system is determined by the turnover rate and the amount of water in the make-up supply. Calculations on a glove box with 2.7% RH make-up supply with a turnover rate of twenty glove box volume per hour result in water vapor concentrations above 5% RH for over just over ten minutes after an influx of

Table IV: Properties of water at 24 °C. Saturated water vapor occurs at 29,210 PPM_V.				
PPM_V	P [Torr]	RH	Density [g/m³]	Mass in 6 m³ [g]
29,210	22.2	100%	21.6	129.6
1000	0.76	3.4%	0.73	4.4 g
10,000	7.6	34%	7.3	43.8 g

moisture such as from a calcination furnace.

One efficient configuration for moisture sorption would be to contain the material in a flat-bottomed, shallow vessel and arrange for a temperature gradient to ensure convection will constantly renew the water in the atmosphere above the material. This configuration is provided during calcination. Magnesium chloride, during cooling, will begin to sorb water at approximately 300 °C. The time during cooling from 300 °C until the material can be handled will result in some moisture sorption. The rate at which water is sorbed should be linear with the water vapor pressure. Ten times more water will be sorbed at a glove box atmosphere of 10,000 PPM_V than at 1,000 PPM_V during this time. After cooling, if the material is kept in the flat-bottomed, shallow vessel used during calcination, additional sorption will occur. During this time a variety of processes will occur. The highly reactive oxide surfaces produced during calcination, such as plutonium oxide, magnesium oxide, etc., will hydroxalate. The salts requiring waters of hydration to be stable in atmospheres with even the smallest amounts of water will react. The hydroxide surfaces will adsorb water depending upon the relative humidity. Adsorbed water may then desorb from the non-reactive surfaces and be available to react to form hydrated salts or hydroxide surfaces with the more reactive components of the calcined material.

There are two reasons to keep the glove box atmosphere RH ALARA (as low as reasonably achievable). The first is to reduce the rate of moisture sorption, which, to a first approximation, will be linear in the water vapor pressure. The second is to limit the amount of water available for sorption. It will take six complete glove box atmospheric replacements to supply the 25 grams of water necessary to exceed the 0.5-wt% criterion in a 1,000 PPM_V atmosphere, whereas in a 10,000 PPM_V atmosphere more than 25 g of water is available.

A final suggestion is to place the freshly calcined material into a container with a lid that will limit convective processes from supplying moisture to the material. Calcined material placed within a container with a lid will rapidly sorb all of the water from the atmosphere within the container, which for a two-liter container would contain at most a few milligrams of water in the container's atmosphere.

Water vapor must then diffuse into the container through any small gaps between the lid and the container as convective processes are prevented by the lid. Even a slip lid container will provide an effective barrier against moisture sorption for days. This has been demonstrated with slip lid cans containing $CaCl_2$ and held in 100% RH conditions resulting in weight gains of 6.1 mg/hr. [33]

ACKNOWLEDGEMENT

BIBLIOGRAPHY

1. "Stabilization, packaging, and storage of plutonium-bearing materials", DOE-STD-3013-2000 U.S. Department of Energy (2000).

2. Mason, R., Allen, T., Morales, L., Rink, R., Hagan, R., Fry, D., Foster, L.., Bender, B., Wilson, E., Martinez, C., Martinez, P., Valdez, M., Hampel, F., Peterson, O., Rubin, and J., Hollis, K., Materials Identification and Surveillance: June 1999 Characterization Status Report, LA-UR-99-3053, Los Alamos National Laboratory !999.

3. Eller, P. G., Mason, R. E., Horrell, D. R., McKee, S. D., Rink, N. A., and Leasure, C. S., Gas pressurization from calcined plutonium oxides, LA-UR-99-3804 Los Alamos National Laboratory 1999.

4. Stakebake, J. L. (1973). "A thermal desorption study of the surface interactions between water and plutonium dioxide." Journal of Physical Chemistry 77(5): 581-586.

5. Zettlemoyer, A. C., F. J. Micale, et al. (1975). Adsorption of water on well-characterized solid surfaces. Water in disperse systems. F. Franks. New York, Plenum Publishing Corporation. 5.

6. Thiel, P. A. and T. E. Madey (1987). "The interaction of water with solid surfaces: fundamental aspects." Surface Science Reports 7: 211-385.

7. Haschke, J. M. and T. E. Ricketts (1997). "Adsorption of water on plutonium dioxide." Journal of Alloys and Compounds 252: 148-156.

8. Haschke, J. M. and T. H. Allen (1999). Interactions of plutonium dioxide with water and oxygen-hydrogen mixtures, Los Alamos National Laboratory.

9. Haschke, J. M. and T. E. Ricketts (1995). Plutonium dioxide storage: conditions for preparation and handling, Los Alamos National Laboratory.

10. Veirs, D. K., J. Morris, et al. (2000). Vapor pressure of water over plutonium dioxide. Plutonium Futures 2000 - The Science, Santa Fe, NM.

11. Haschke, J. M. (1995). Reactions of plutonium and uranium with water: kinetics and potential hazards, Los Alamos National Laboratory.

12. Haschke, J. M., T. H. Allen, et al. (1999). Reaction of plutonium dioxide with water and oxygen-hydrogen mixtures: mechanisms for corrosion of uranium and plutonium, Los Alamos National Laboratory.

13. Schulze, R. K., J. D. Farr, et al. (2000). "Water interactions at plutonium oxide: surface chemistry." Abstracts of Papers of the American Chemical Society 219: 112.

14. Lide D. R. Ed. (1996). "CRC Handbook of Chemistry and Physics 77th Ed", CRC Press Boca Raton, Pg. 15-25.

15. Bell L. N. and Labuza T. P. (2000). "Moisture Sorption: Practical Aspects of Isotherm Measurement and Use, 2nd Ed.", American Association of Cereal Chemists, Inc. St. Paul, pgs 33-37.

16. Bukovec, N., Bukovec, P., and Arbanas, V., "TG and DSC investigation of $CaCl_2 \cdot 6H_2O$, a phase change material for energy storage." Thermochimica Acta 148: 281-288 (1989).

17. Lawrence, A. D., Bu, J., "The reactions between Ca-based solids and gases representative of those found in a fluidized-bed incinerator", Chem. Eng. Sci. 55, 6129-6137 (2000).

18. Morales, L., Gallegos, U., and Barney, S., "Thermal gravimetric analysis with moisture detection systems for water determinations: a study on selected 3013 materials", LA-UR-02-3728, Los Alamos National Laboratory, 2002.

19. Perry, G. S., and Fletcher, H., "The $MgCl_2$-KCl-$CaCl_2$ phase diagram", Thermochimica Acta 217, 277-284 (1993).

20. Clegg, S. L., Pitzer, K. S., and Brimblecombe, P., "Thermodynamics of multicomponent, miscible, ionic solutions. 2. Mixtures including unsymmetrical electrolytes", J. Phys. Chem. 96, 9470-9479 (1992).

21. Pabalan, R. T., and Pitzer, K. S., "Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO_4-OH-H_2O", Geochimica et Cosmochimica Acta 51, 2429-2443 (1987).

22. Carrott, M. M. L. R. and P. J. M. Carrott (1994). "Adsorption of water-vapor by microporous magnesium-oxide." Studies in Surface Science and Catalysis 87: 497-506.

23. deLeeuw, N. H., G. W. Watson, et al. (1995). "Atomistic simulation of the effect of dissociative adsorption of water on the surface-structure and stability of calcium and magnesium oxide." Journal of Physical Chemistry 99: 17219-17225.

24. deLeeuw, N. H., G. W. Watson, et al. (1996). "Atomistic simulation of adsorption of water on three-, four-, and five-coordinated surface sites of magnesium oxide." Journal of the Chemical Society-Faraday Transactions 92: 2081-2091.

25. Ferry, D., A. Glebov, et al. (1996). "Observation of the 2nd ordered phase of water on the MgO(100) surface: low-energy-electron diffraction and helium atom scattering studies." Journal of Chemical Physics 105: 1697-1701.

26. Wu, M. C., C. A. Estrada, et al. (1996). "Model surface studies of metal-oxides: adsorption of water and methanol on ultrathin MgO films on Mo(100)." Journal of Chemical Physics 96: 3892-3900.

27. Johnson, M. A., E. V. Stefanovich, et al. (1999). "Dissociation of water at the MgO(100)-water interface: comparison of theory with experiment." Journal of Physical Chemistry B 103: 3391-3398.

28. Kirsh, Y., S. Yariv, et al. (1987). "Kinetic analysis of thermal dehydration and hydrolysis of MgCl2*6H2O by DTA and TG." Journal of Thermal Analysis 32: 393-408.

29. Garvin, D., Parker, V. B., and White, Jr., H. J., Editors, "Codata Thermodynamic Tables: Selections for Some Compounds of Calcium and Related Mixtures: A Prototype Set of Tables" Hemisphere Publishing Corporation, Washington, ISBN 3-540-17788-4 (1988).

30. Galwey, A. K. and G. M. Laverty (1989). "The thermal decomposition of magnesium chloride dihydrate." Thermochimica Acta 138: 115-127.

31. Danes, F. E., S Mason, R., T. Allen, et al. (1999aint-Aman, E., and Coudurier, L., (1988) "Etude Thermodynamique de la Decomposition Thermique des Hydrates du Chlorure de Magnesium", Journal of Thermal Analysis 34, 821-833.

32. E. Bluhm, "Moisture Uptake on Impure Residues", MIS Working Group Meeting, March 2001.

33. Bates, C. and Russell, C (2001). "Improvements to AWE's Packaging Specification for Interim Storage of Plutonium-Containing Residues", Packaging JOWOG October, 2001.