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Hydration of Plutonium Oxide and Process Salts, NaCl,
KCl, CaCl$_2$, MgCl$_2$: Effect of Calcination on Residual
Water and Rehydration

Chemical Science and Technology and Nuclear
Materials Technology Divisions

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Executive Summary

This report summarizes the answers to questions related to proposed changes to the new DOE plutonium storage standard[1]: What are the effects of lowering the calcination temperature from 950°C to 800°C on dehydration of PuO$_2$ and the salts NaCl, KCl, MgCl$_2$ and CaCl$_2$? What are the rehydration rates of these materials as a function of time and humidity?

Based on the lack of published quantitative data specifically dealing with the hydration behavior of air-calcined samples and the diversity of stored samples, it is difficult to quantify how much water remains after calcination in air at 800°C or 950°C. The term water here and in subsequent sections will also include surface hydroxides. While it is likely a sample calcined at 800°C contains less than 0.5 wt % water, there is no published literature that will conclusively support this conclusion. All available information does suggest that lowering the calcination temperature from 950°C to 800°C will result in a higher water content.

Quantitative information for air or inert atmosphere-calcined samples is limited to: Studies on the NaCl/KCl/MgCl$_2$ fused salt indicate that after heating under argon above 800°C, the salt contains 0.22 wt % water.[2] For PuO$_2$, calcining at 700°C lowers the water content to less than 0.2 wt % and calcining at 950°C removes all detectable water.[3] Pure CaCl$_2$, dried at 850°C with periodic flushes of HCl, still may contain 0.2-0.3 wt % water.[2]

The most important consequence of lowering the calcination temperature to 800°C is the increase in surface area and water sorption potential. The best way to minimize water sorption is to minimize the surface area, optimally via melting. Since 800 ¡C is only 20 ¡C above the melting point of CaCl$_2$, the most problematic constituent, the actual temperature of the salt residue in the calcination furnace may be below the CaCl$_2$ melting point. This can be remedied by ensuring the lowest temperature in the calicination bed is greater than or equal to 800°C.

Regarding the rate of adsorption of water by the salts and oxides of interest, the lack of quantitative information makes it impossible to estimate the time required for a sample to adsorb enough water such that it no longer meets the less than 0.5 wt % water content criteria. However, some generalities can be made. Adsorption of surface water will happen in the presence of even the smallest amount of water. The extent of the adsorption will depend on the specific composition of the sample and the ambient relative humidity. Larger surface areas (as a result of process conditions including crushing the sample after calcination) will increase the area available for adsorption. To exceed the 0.5 wt% water criterion, however, the surface area of NaCl (assuming monolayer coverage of water) would need to be 25 m^2/g. Because of their hygroscopic nature, high concentrations of $CaCl_2$ and $MgCl_2$ will also result in increased water adsorption. For samples containing $CaCl_2$ and $MgCl_2$ it is especially important to keep the humidity of the glovebox below 35% as $CaCl_2$ deliquesces at that humidity. CaO and MgO, formed via hydration and calcination of $CaCl_2$ and $MgCl_2$ respectively, probably will not present a problem. Using Haschke's measurement of 2 monolayers of water present on PuO_2 at humidities between 1% and 50%, if a sample with surface area 5 m^2/g or less (obtained by calcining at 950°C or higher) had complete monolayer coverage, this corresponds to 0.18 wt % water. Calcining at 800°C (surface area between 6-8 m^2/g) would raise the water content value from a double hydration layer to 0.26 wt %.

References:
1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage, "DOE-STD-3013, U.S. Department of Energy, **1996**.

2. Fife, K. W.; Bowersox, D. F.; Christensen, D. C.; Williams, J. D. "The Preparation of Fused Chloride Salts for Use in Pyrochemical Plutonium Recovery Operations at Los Alamos," Los Alamos National Laboratory, **1986**.

3. Haschke, J. M.; Ricketts, T. E. *Journal of Alloys and Compounds* **1997**, *252*, 148-156.

In addition, the following books were read and were found to contain no relevant information:

1. Advances in Molten Salt Chemistry. Eds. J. Braunstein, Gleb Mamantov, and G. P. Smith; Plenum Press, New York.1971.

2. The Chemistry of Molten Salts: An Introduction to the Physical and Inorganic Chemistry of Molten Salts and Salt Vapors. Harry Bloom; W. A. Benjamin, Inc., New York. 1967.

3. Comprehensive Treatise of Electrochemistry: Vol. 5, Thermodynamic and Transport Properties of Aqueous and Molten Electrolytes. Eds. Brian E. Conway, J. O'M. Bockris, and Ernest Yeager; Plenum Press, New York. 1983.

4. Modern Aspects of Electrochemistry No. 2; Ed. J. O'M. Bockris; Academic Press Inc., New York. 1959.

5. Modern Aspects of Electrochemistry No. 9; Eds. B. E. Conway and J. O'M. Bockris; Plenum Press, New York. 1974.

6. Molten Salt Chemistry. Ed. Milton Blander; Interscience Publishers, a division of John Wiley & Sons, New York. 1964.

7. Molten Salts Handbook. George J. Janz; Academic Press, New York. 1967.

8. Physical Properties Data Compilations Relevant to Energy Storage. II. Molten Salts: Data on Single and Multi-Component Salt Systems. G. J. Janz, C. B. Allen, N. P. Bansal, R. M. Murphy, and R. P. T. Tomkins; U. S. Department of Commerce. NSRDS-NBS 61 Part II. April 1979

Hydration of Plutonium Oxide and Process Salts, NaCl, KCl, CaCl$_2$, MgCl$_2$: Effect of Calcination on Residual Water and Rehydration

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Abstract

This report contains a review of the literature on the dehydration and rehydration of PuO$_2$, NaCl, KCl, CaCl$_2$, and MgCl$_2$, experimental results on the dehydration and rehydration of materials containing PuO$_2$ and these salts, and recommendations regarding the calcination temperature and atmospheric conditions required to minimize sorbed water.

Introduction

Some plutonium dioxide residues in the DOE complex contain significant quantities of chloride salts. These residues may be put into long-term storage if they can meet the criteria of the pertinent standard (DOE-STD-3013-96 or the new standard) which requires the residue to have less than 0.5 wt % water content.[1] (The use of the term water herein applies to both physisorbed water and chemisorbed hydroxides.) There is concern that with time these containers may become pressurized due to the formation of gases via multiple processes, including catalytic and radiolytic decomposition of H$_2$O, potentially leading to container rupture, plutonium dispersion, and other hazards. To minimize the water in storage containers the oxide and salt mixtures (also referred to as impure oxides) will be calcined prior to packaging. The current standard requires salts for storage to be calcined in air at 950°C; however, the lower calcination temperature of 800°C is being considered. Once calcined, the oxide and salts may be

kept in a glovebox or processing apparatus until packaging, allowing for potentially problematic rehydration. This report summarizes the literature available that helps address: What are the effects of lowering the calcination temperature on dehydration of PuO_2 and the salts NaCl, KCl, $MgCl_2$ and $CaCl_2$? Specifically, will impure oxides still meet the 0.5 wt% water requirements? What are the rehydration rates of these materials as a function of time and humidity?

Dehydration and Rehydration of PuO_2

Haschke has published several reviews discussing the interaction of plutonium dioxide with water.[3, 5] This section summarizes his work and includes reports by other authors not discussed in his reviews.

Stakebake performed a gravimetric desorption experiment (heating a sample under vacuum at successively higher temperatures and monitoring mass changes) and determined that water is removed from the surface of PuO_2 stepwise.[6] He suggested most of the physically adsorbed water (67% of the total water) can be removed at room temperature, while the remaining 33% of water which is distributed between two chemisorbed phases is not removed until temperatures close to 1000°C. At 800°C 2 mg of water per g of PuO_2 (0.2 wt%) remained on the surface.[6] In a later paper, Stakebake reports results from thermal desorption experiments (heating a sample under vacuum at successively higher temperatures while determining the composition the off-gas using a time-of-flight mass spectrometer). In these experiments, one species is desorbed starting at 100°C and a second species is starting to be removed at 300°C. Total water desorption, within limits of detection, is accomplished around 700°C.[7] Both the gravimetric and thermal desorption experiments indicate water is adsorbed onto a plutonium dioxide surface in two ways, chemi- and physisorbed. However, there is no discussion as to why these two different desorption techniques give such different temperatures for complete water removal.

Haschke contends the amount of water remaining after calcination at 800°C or lower depends on the how the plutonium dioxide was made.[3, 5] However, after heating to 950°C oxides produced from both metal hydride and metal oxalate contain no detectable water as determined by loss on ignition (LOI) tests (measures mass loss after a sample is heated). The following table summarizes his results from LOI tests on two different PuO_2 samples:

Table 1. LOI Results for Oxides Calcined at Different Temperatures[3]

Calcination Temperature (°C)	Oxide from Metal-Hydride-Air		Oxide from Oxalate Calcination	
	Mass lost (±0.02%)	Surface Area (m^2/g)	Mass lost (±0.02%)	Surface Area (m^2/g)
As received	0.52%	11.3	0.97%	29.3
600	0.16%	10.2	0.57%	23.9
700	0.05%	8.1	0.09%	5.7
800	0.03%	7.9	0.14%[a]	5.8
950	0.00%	4.8	0.00%	2.7

[a] The anomalous result at 800°C is attributed to an error arising from exposure to moisture during handling or from inaccurate LOI analysis.

Notably, the calcination temperature of 700°C appears to reduce moisture content below 0.1 wt % for both types of PuO_2. Some uncertainty is introduced by the anomalous result at 800°C reported for the oxide from the oxalate calcination. The problem may not be in the measurement at 800°C but the measurement at 700°C, suggesting the moisture content at 700°C may be above 0.1 wt % for this oxide. Additional experiments are needed to address this question.

Several authors report different amounts of water adsorption on plutonium dioxide. Stakebake reports approximately 9 mg H_2O (0.9 wt %) adsorbs at 27°C per g of PuO_2 at the highest humidity measured, 24 torr. When the water is desorbed by lowering the humidity and then the adsorption experiment is repeated by increasing the humidity, the adsorption is not reversible, implying some of the water is chemisorbed. After eight cycles of fluctuating humidity between 0 and 24 torr of water, the total water adsorbed (at the highest humidity) was found to be approximately 20 mg H_2O (2 wt %) per g of PuO_2.[6]

Caldwell and Menis studied water adsorption on PuO_2 samples calcined at 350, 490, and 760°C (as cited in reference 1). The sample calcined at 760°C adsorbed the least amount of water, approximately 1 mg H_2O per 1 g sample (0.1 wt %) at room temperature under conditions of less than 50% humidity. The relatively low adsorption was attributed to a relatively small surface area resulting from a relatively high calcination temperature indicating the method of

preparation of the oxide is important. Moseley and Wing report a much higher surface coverage of water on plutonium dioxide (as high as 50 mg H_2O (5 wt %) per g PuO_2), but they used uncalcined samples (implying a larger surface area).[8]

Haschke's report of the time dependence of water adsorption on PuO_2 samples (Table 3) supports the conclusion that the hygroscopic character of bulk PuO_2 strongly depends upon the method of preparation.[3] In Haschke's experiments, the oxides from hydride and oxalate samples were placed in 1% and 10% relative humidity environments, respectively. For the hydride samples, the adsorption equilibrium was reached after two hours; however, the sample calcined at 700°C adsorbed more water per g of material than the one calcined at 950°C. After normalizing for surface area, the values are actually the same (approximately $0.16 mg/m^2$). The same adsorption rate despite different surface areas indicates the 0.05 wt % remaining in the sample after calcination at 700°C is not surface physisorbed, but chemisorbed. A second monolayer of water begins to adsorb at humidities greater than 1% with complete coverage by 20% relative humidity. For a sample with a surface area of 5 m^2/g or less (obtained by calcining at 950°C), a two monoloayer coverage corresponds to 0.18 wt% water.[3, 5] Calcining at 800°C results in a surface area of 6-8 m^2/g and would raise the water content to 0.26 wt%. From 20% to 50% relative humidity no additional adsorption appears to take place. Over 50% relative humidity, additional water adsorbs at a faster rate.[3, 5]

Haschke's conclusions are: 1) temperatures in excess of 900°C are necessary to totally remove adsorbates and residues (within limits of detection), 2) humidity levels required to initiate adsorption have not been defined (because adsorption has already taken place in environments where humidity is 1% or higher), and 3) prevention of re-adsorption during handling is virtually impossible. For PuO_2 he concludes that a reduction in relative humidity from 50% to 1% only decreases coverage from two monolayers to one, and significant reduction in coverage is only achieved by maintaining an atmosphere below 0.3% relative humidity (RH) (i.e. 100 ppm H_2O).[3, 5]

The United Kingdom Aldermasten facility criteria for 5-yr storage of PuO_2 in food-pack cans specifies the use of a <100 ppm H_2O glovebox atmosphere during packaging of material calcined

at 400°C. Under these conditions, they report no pressurization problems resulting from water adsorbed onto PuO_2.[31]

The rate of water adsorption by calcined plutonium oxide depends on process history, surface area, relative humidity, and time. Experiments by Haschke suggest adsorption occurs in discrete steps.[3, 5] The first step involves half a monolayer of water and its rate is determined by atmospheric humidity. The rate of second and subsequent steps is determined by the concentration of vacant adsorption sites remaining in the adsorbate layer. The longer the sample is exposed to moisture, the greater the penetration of the moisture into the sample and subsequently, the greater the amount of water adsorbed. Powdered oxide (2 gm/cm^3 bulk density) is penetrated to 10 cm in 3.7 h at 50% relative humidity.[5]

Dehydration of the Common Processing Salts, NaCl, KCl, $CaCl_2$, $MgCl_2$

Prior to being packaged for storage, plutonium oxide and impure oxide residues will be calcinated in air at high temperature (800°C or 950°C). Heating $MgCl_2$ and $CaCl_2$ under these conditions can result in the formation of MgO and CaO, respectively. The relative ratios of salt and oxide dependent on the amount of water present. Thus, MgO and CaO may be present in the oxide residues, and the hydration behavior of MgO and CaO must also be considered. The salts will be discussed in two categories, the relatively non-hygroscopic NaCl and KCl, and the hygroscopic $MgCl_2$ and $CaCl_2$ along with their oxides.

For NaCl and KCl, there is little published information regarding the amount of water remaining after heating at high temperature in air. Duval *et al*. report the TGA curves for 300mg samples of NaCl and KCl (prepared by the reaction of the appropriate alkali carbonate with HCl) reach horizontal (implying no more water loss) at 407° and 219°C, respectively.[32] (Atmosphere of TGA acquisition not given). The authors mention TGA data varies depending on the sample size (larger samples require higher temperatures to stabilize), ambient atmosphere, and the heating rate. In addition, stabilization of a TGA curve alone is not sufficient proof of complete dehydration; the absence of water should also be confirmed by a second analytical method. In the author's discussion of TGA curves, no secondary analysis is mentioned.[32]

Some reports regarding the drying of NaCl and KCl using vacuum techniques and inert gas atmospheres have been published. Most of the hydrated water can be removed by heating to around 200°C under vacuum. Removing the last traces of residual moisture from the salts requires more rigorous methods. One study showed that NaCl and KCl could be completely dried at temperatures as low as 420°C and 300°C, respectively, if the salts were heated in dynamic vacuum (water content determined by LOI tests). Periodic flushing with an inert gas during the process hastens the removal of water vapor.[10]

Barraclough used IR spectroscopy to show that heating NaCl under vacuum to 350°C removed all of the IR bands in the 3000-4000 cm-1 region.[11] At higher temperatures the salt will react with ambient water vapor to form hydroxides (hydrolysis). Kaufmann, without any experimental details, suggests this decomposition represents only about 0.06% of the total NaCl, although he contends the actual extent is dependent on the concentration of the water vapor.[12] Otterson reports that hydroxide concentration on NaCl surfaces occurs in various amounts under different conditions with the highest ratio for NaCl crystals fused in air.[13] Barr *et al.* determined that if NaCl crystals are heated to 700°C for 1 to 7 days in an N_2 atmosphere with 1% relative humidity, then one observes a 1×10^{-4} mole fraction concentration of hydroxide based on chloride displacement. For a sample heated in neon at 450°C in 2% relative humidity, he reported that 50 atomic layers of NaCl are converted into NaOH .[14] It should be noted that this extent of reaction is unexpected considering the equilibrium constant for the reaction, $NaCl + H_2O \rightleftharpoons NaOH + HCl$, in the bulk phase is 10^{-23} at 500°C.

The Gmelin Handbook states that in a closed vessel NaCl doesn't react with the water in air until 850°C, although in an open vessel the reaction occurs at an earlier temperature. The reaction rate is diffusion limited and steadily increases with temperature until about 950°C when the rate decreases with time due to changes in conditions for diffusion.[9]

Maricle and Hume studied drying procedures of equimolar NaCl-KCl via polagraphy and found that fusing ordinary dry salts (around 750°C) in air followed by a 20-min purge with Ar resulted in a small amount of hydroxide formation (hydroxide concentration estimated at 0.17 mmol or 3×10^{-4}% water). If rigorously dried HCl was bubbled through the NaCl-KCl melt

before the Ar flush, the hydroxide was converted back to the chloride and the small hydroxide impurity was removed. They showed that even non-pre-dried salts and hygroscopic salts like LiCl could be effectively dried if Cl_2 gas was passed through immediately after fusion followed by an Ar flush.[15] Other reports recommend drying under vacuum or an inert atmosphere to prevent the reaction of salt with water vapor.

Only one study, by Fife *et al.,* gives a quantitative value for water concentration in a mixed fused salt. A mixture of $NaCl/KCl/MgCl_2$ (wt %: 27.2%/34.8%/38.0%) was made by fusing $KCl/NaCl$ with $MgCl_2$ (not pre-dried) at high temperature (actual temperature not given but assumed to be above the melting point) with an Ar sparge. The sample was cooled and stored under vacuum. After cooling, the salt was determined (by an undisclosed procedure) to contain 0.22 wt. % H_2O.[2] Based on the work by Maricle and Hume, the amount of water present in this mixed $NaCl/KCl/MgCl_2$ salt is most likely only a function of the initial concentration of $MgCl_2$. Unfortunately, there is some uncertainty as to the reliability of the water content value because no information is given as to when the testing for water took place, what the surface area of the salt was (large chunks, crushed powder, ...) or how long and under what conditions the samples were stored (i.e. Is the water content due to water adsorbing after the sample cooled? Or is it water that was not driven off during the heat treatment?).

Two methods for drying hygroscopic calcium chloride, both more rigorous than drying methods for NaCl, KCl, and $MgCl_2$, were examined by Fife *et al.* The first method involves heating $CaCl_2$ under vacuum for 5-7 days at 100°C, then raising the temperature to 225°C for 5-7 more days. The salt is stored in plastic bags and pressed into cylinders to reduce surface area. The second method involves melting $CaCl_2$ at 850°C under Ar, followed by sparging with HCl for 30 minutes to dry the salt and convert oxide impurities to chlorides. The system is then sparged with Ar to purge the HCl and allowed to cool. Even when subjected to these rigorous drying procedures, salts from both processes contained approximately 0.3 wt% H_2O.[2] (No information was given on when the salts were analyzed.)

Other authors discuss more rigorous methods used to dry $CaCl_2$ but do not quantify the amount of water remaining in the salt. Kondo *et al* dried $CaCl_2$ by slowly heating the sample in N_2 to 397°C where they kept the salt for 18hrs.[16] They provide no evidence that the salt is

completely dried but use it for their studies on the hydrolysis of fused calcium chloride at high temperatures. They were studying the feasibility of the following two reactions:

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2HCl \quad and \quad CaCl_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HCl$$

Both reactions have relevance to what species are present after calcination at 800°C and 950°C. Although calcium hydroxide is unstable above 577°C (decomposes to form CaO and H_2O), it may still be present at higher temperatures because it is soluble in calcium chloride. Kondo *et al* cite a freezing point diagram for the $CaCl_2$-CaO system that has a eutectic at 593°C corresponding to 28.8 mole percent CaO.[16] The binary phase diagram for $CaCl_2$-CaO published by Wenz *et al* shows the eutectic to be at 750°C corresponding to 6.5 mole percent CaO.[17] The reasons for the differences in the eutectic points and concentrations of CaO in the two reports are not clear. However, both diagrams clearly indicate some CaO is soluble in $CaCl_2$.

Kondo and co-workers bubbled H_2O/N_2 vapor through $CaCl_2$ and measured the weight loss and Cl_2 evolution at various temperatures.[16] The higher the temperature and the higher the partial pressure of H_2O, the larger the weight loss observed. When the flow gas contained 12 to 24% moisture by volume, a maximum of 0.2 mole percent of CaO was formed at 900°C and 950°C. At 810°C, with low moisture content (13 to 19%) CaO is formed, while at higher moisture content (>24%) both CaO and $Ca(OH)_2$ are formed.[16] This study indicates that for salts containing $CaCl_2$, the calcination products could contain CaO and $Ca(OH)_2$ depending on the ambient humidity, $CaCl_2$ concentration and temperature.

Arbanas *et al.* reports the effects of dehydration on $CaCl_2 \cdot 6H_2O$ mixed with a small amount of NaCl or KCl.[18] The authors find that an appropriate amount of salt additive can increase the stability of the intermediate hydrates during thermal dehydration and change the stoichiometry of the dehydration process. Unfortunately, the authors do not provide details and the majority of the results are presented in a table discussing weight loss as a function of moles of water for various combinations of salt as measured by thermogravimetric (TG) and differential scanning calorimetry (DSC) methods in dry air over a temperature range of 100-300°C. Their largest water loss, 6.38 moles H_2O, comes from the dehydration of a mixture of 94.4% $CaCl_2 \cdot 6H_2O$,

5.1% KCl and 0.5% NaCl. They do not discuss where the extra 0.38 moles of water might originate.[18]

According to Gmelin, $MgCl_2$ is the most hygroscopic of all the alkaline earth chlorides.[19] Similar to $CaCl_2$, if $MgCl_2$ is heated in air that contains water vapor, magnesium oxide will form. Between 350° and 505°C, the reaction follows $MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$; above 505°C, the reaction is $MgCl_2 + H_2O \rightleftharpoons MgO + HCl$ although neither reaction goes to completion.[19] Heating to high temperatures removes most, but not all, of the water found in magnesium chloride. In the vapor above a sample of $MgCl_2$ that has been heated to 800°C and 900°C (exact conditions not given), 0.0127 and 0.0086 atms of water, respectively, are detected. $MgCl_2 \cdot H_2O$ can be completely dehydrated by heating the salt to 200°C in a HCl atmosphere.[19]

The conversion of $MgCl_2$ to MgO will decrease the amount of water present. Xia *et al.* determined the thermal behavior of magnesium oxychlorides ($xMg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, $x = 3$ or 5) and found that the oxychlorides convert to MgO at temperatures above 450°C. Although magnesium oxychlorides are unlikely to be present in residues intended for long-term storage, this report is useful because it discusses the water content of MgO above 500°C. No transitions are observed in DTA curves from 500 to 1300°C, indicating no water is present in the MgO.[20] Coluccia *et al.* adsorbed water on a MgO surface and then heated the sample to determine at what temperature all the water is removed. After surface water has been removed by vacuum at room temperature, 1.2 monolayers of water remain according to IR measurements. All molecular water is removed by 100°C leaving only a hydroxide monolayer that is partially decomposed via water evolution at 200°C. At 400°C only 0.25 of the hydroxide monolayer remains and by 800°C no water is observed by IR spectroscopy.[4] It is not clear why the DTA and IR studies performed by these two groups give different results. One can conclude that at temperatures greater than 800°C MgO contains no detectable water.

Rehydration of the Common Processing Salts, NaCl, KCl, CaCl$_2$, MgCl$_2$

The most abundant amount of salt hydration information concerns NaCl primarily because of its importance in atmospheric chemistry and in industry. An entire book on NaCl has been written by the chief chemical engineer of the International Salt Company, Dale Kaufmann. According to Kaufmann, water concentration in normal mined salts range from 0 to 0.4 weight percent and is a function of surface area. Moisture on the surface is mainly due to H$_2$O sorbed from the air or the mother liquor. And regardless of how dry the salt seems or how high the drying temperature, Kaufmann claims a film of saturated brine is always present on the salt surface. Additional water will adsorb according to the humidity conditions. When salt is in contact with air that has a partial vapor pressure of water greater than that of the saturated brine layer, additional water will adsorb onto the surface. The absorption will continue until the vapor pressure of the saturated brine exceeds the partial pressure of the water or until the salt is entirely dissolved. Critical relative humidity (cRH) is defined as the partial pressure of water required for deliquescence (the point at which salt begins to dissolve) and for NaCl this is 75% relative humidity.[12] This value is confirmed in several other reports. [4,10,21-23] Water can be desorbed from the brine film as well by the opposite of the above-described process. Therefore, if the water content in air is less than 75% relative humidity, the salt, if damp, will dry out and if dry already, the salt will remain dry.[12] Water adsorption as a function of time not reported in Kaufmann's book.

Innes studied the adsorption of water onto sodium chloride by measuring weight changes in atmospheres of uncontrolled temperature (12-20°C) and various humidity. He observed no changes in weight from initial values for samples held at humidities of 65, 70 and 75% over a 10-week period. At 80% relative humidity the weight gain was 0.14% over a 10-week period, indicating that near the deliquescence point the rate of dissolution is fairly slow.[21]

Other authors later would argue that although Innes saw no weight change at humidities from 65-75%, water was still present on the surface. Barraclough determined the water vapor adsorption isotherms on a sample of NaCl at 25°C. He allowed equilibration times of at least two hours at each data point. The isotherm had a sharp step at a relative humidity (RH) of 35%, proceeded by a knee, and at a relative humidity of 76%, the amount adsorbed continued to increase at constant pressure. The adsorption was completely reversible, indicating water does

not penetrate into the lattice. The step at 35% RH is indicative of the absorption of a full monolayer of water. [11] Peters and Ewing report the same type of water adsorption properties in their study of NaCl surfaces using IR spectroscopy. They claim that at 40% relative humidity the water monolayer produces no solvation of surface cations and/or anions, but between 40 and 50% relative humidity surface ions are beginning to be solvated.[23]

Dai and Salmeron used atomic force microscopy to study water adsorption on NaCl crystals at varying humidity.[24] They contend that exposure to humidities around 35% results in the formation of a monolayer of water, but that at lower humidities submonolayer amounts of water are also present on the surface, concentrated around steps and edges. Above 35% humidity, surface ions are hydrated and become mobile.[24]

One of the few references to water adsorption on KCl is a study by Luna *et al.*[25] They measured the amount of water adsorption using scanning polarized force microscopy on KCl and NaCl. For KCl they determined the relative humidity for initial solvation of surface cations (corresponding to one monolayer of water on the surface) was 66% and the deliquescence point was 87% relative humidity. For NaCl, like the previous reports, the initial solvation step was observed at 40% relative humidity and deliquescence at 73%. For NaCl, they determined that at relative humidity around 37.5% surface concentration of solvated cations is on the order of 1% of the surface density. For cations to be freed from the lattice it would require six molecules of water for one NaCl molecule and five water molecules for one KCl molecule.[25]

In another report, the amount of water adsorption on KCl was measured by ellipsometry.[26] Here, Bayh and Pflug determined that water adsorbs in a stepwise manner and continues to do so even at high humidities. Initial measurements, before the salt was exposed to water vapor (no information given on what initial humidity was or how the salt was stored) indicated a single monolayer of water is present on the surface of KCl at room temperature. They determined that by 60% relative humidity KCl has 40Å (10 monolayers) of water on the surface.[26] These results indicate a greater water content for KCl than other reports; however, there is no discussion of the apparent discrepancies.

While the deliquescence point (i.e. cRH) for pure salts is relatively high, combinations of salts have a lower cRH than the pure components. Tang *et al.* determined the cRH for an equimolar

NaCl/KCl mixture to be 72% at 25°C while the cRH for NaCl is 75% and for KCl is 82%.[27] Likewise for NaCl containing $MgCl_2$ (cRH not given) or $CaCl_2$ (cRH = 35% at RT), the critical relative humidity will be lowered, the exact value dependent on the amount of $MgCl_2$ or $CaCl_2$ present. The level of sorption or desorption will vary depending on the mixture and the surface area of the particles.[12] No other information was discovered concerning the adsorption of water onto the surfaces of KCl, $CaCl_2$, or $MgCl_2$.

Maciel-Camacho *et al.* studied the hydration kinetics of lime after calcining $CaCO_3$ pellets in air at 750, 850, 1010, and 1100°C to produce CaO pellets with different porosities and surface areas.[28] The CaO pellets were then hydrated under different mixtures of water vapor in air. Calcium oxide hydration involves the heterogeneous reaction of CaO with water at the solid/liquid interface to form calcium hydroxide according to: $CaO + H_2O \rightleftharpoons Ca(OH)_2$ + heat. Experimental results show the pellet with the lowest calcination temperature showed the greatest hydration rate, about .8 fractional hydration in 600 minutes at partial water pressure of 2.8 kPa, owing to the relatively large surface area of the pellet. (The fractional hydration is defined as the ratio of the weight loss or gain, $\Box W$, at any time *t*, to the change of weight corresponding to complete reaction, $\Box W_t$. Likewise, higher humidity resulted in larger fractional hydrations over the same time period).[28]

Holt et al studied surface modifications of MgO exposed to water vapor using atomic force microscopy.[29] They found MgO to be relatively inert to water adsorption at relative humidities less than 30%. Above 30%, degradation of the sample was observed at sites of low coordination (corners and steps). The change was gradual and differences were observable after 12 hours. Exposure to 100% humidity for times as brief as 10 minutes resulted in extensive dissolution of the surface.[29] The general experimental consensus is that MgO surfaces adsorb water associatively in monolayer coverages and dissociatively at defect sites to form surface hydroxyl groups. Associatively bound water can desorb upon decreasing humidity; however, the hydroxyl groups on the surface of MgO will not desorb. Only heating to higher temperatures (>200°) will begin to remove the surface hydroxyl layer.

Quantitatively, Stirniman found that a monolayer of saturation coverage corresponds to approximately one water molecule per surface unit cell of MgO.[30] Coluccia et al conclude that if

all sites are occupied (implying one water molecule per each Mg atom), then a monolayer of water corresponds to 12 H_2O molecules per 100 $\text{\textcircled{1}}^2$ (1.2×10^{15} molecules per cm^2) of surface area.[4] In terms of a weight percent, this corresponds to 0.36 mg H_2O per m^2 of surface area. This implies for MgO to adsorb enough water to contain greater than 0.5 wt% water (monolayer coverage), the surface area would need to be greater than 14 m^2/g. Coluccia provides the only experimental results by determining that a MgO pellet left in contact with water vapor (2.14 kNm^{-2}) for 40 minutes adsorbed 29 water molecules per 100 $\text{\textcircled{1}}^2$ corresponding to 2.4 monolayers of water.[4]

Summary of Water Interactions with Impure Plutonium Oxides Containing NaCl, KCl, MgO, and Hydrated CaCl$_2$

The Materials Identification and Surveillance (MIS) project of the DNFSB 94-1 Research and Development Program at Los Alamos National Laboratory has characterized a variety of pure and impure plutonium oxides that have been in storage for up to twenty years. Recent experiments involve impure oxides containing up to 18 % chlorine by elemental analysis. The exact chloride containing phases were identified by x-ray powder diffraction. The impure oxides used were ARF 365, which contained NaCl and KCl, and N002a and 03038, which contained NaCl, KCl, MgO and CaCl$_2$. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were used to study thermal stability, particularly the removal and re-adsorption of water and the vaporization and/or decomposition of inorganic salts. The initial TGA/DTA experiments were conducted concurrently on the mg scale with oil-free bottled air. The temperature was ramped from 25 to 1000° C at 10 °C/min. Additional TGA/DTA experiments were performed in Ar (standard grade, no additional purification), or in a separate tube furnace in air.

For the three materials, ARF365, N002a, and 03038, the loss on ignition (LOI) after heating to 1000°C in air was 13.8 mass %, 18.2 mass % (an average of three runs), and 18.7 mass %, respectively (Table 2). The ARF365 sample lost approximately 2 mass % (assuming all water was lost between room temperature and 200°C) due to the removal of water. The balance of the removed mass % was largely due to the vaporization of inorganic salts (assuming all water is

removed by 200°C). For N002a and 03038, removal of water accounted for approximately 9 mass %; the balance was largely due to the removal of the inorganic chlorides. The TGA for ARF365 indicates a single heating of mg quantities to 1000°C for less than two hours is sufficient to remove water and salt impurities. This was not the case for N002a and 03038; these materials had to be heated to 1000°C in a separate tube furnace for 48 hours before they were thermally stabilized and showed no additional mass loss (all water and salt impurities are removed).

Table 2.   Loss On Ignition (LOI) Test Results for ARF365, N002a, and 3038

Sample	Composition of chloride phases present in sample	LOI Result (1000°C)
ARF 365	NaCl, KCl	13.8%
N002a	NaCl, KCl, $CaCl_2$	18.2%
03038	NaCl, KCl, $CaCl_2$	18.7%

The re-adsorption of water on samples of ARF 365, N002a, and 03038 was also investigated. DTA curves (obtained before any salt impurities were removed from the sample) for ARF 365, shown in Figure 1, serve as an example. The solid curve represents the initial DTA run for a sample as obtained from the storage container. All four thermal events are attributed to the removal of water. This graph indicates the sample stayed relatively dry during storage. The dashed curve is the DTA measured the next day after the sample had cooled overnight in flowing Ar. The first thermal event is enhanced and second and third thermal events are slightly shifted, indicating water re-adsorbed onto the surface (the source of the re-adsorbed water was most likely the Ar stream). DTA experiments (not shown) indicate water re-adsorption is greatly reduced for ARF 365 samples that are initially heated to 1000°C for two hours (to remove salt impurities). The results for N002a and 03038 are similar but more dramatic. Figure 2 shows three DTA curves for N002a. The solid curve corresponds to the initial removal of water from a sample as obtained. Here the initial amount of water is greater (as expected since the sample contains the more hygroscopic $CaCl_2$). The dashed curve shows the removal of re-adsorbed water after that sample was allowed to cool overnight in flowing Ar. The thicker dashed curve was obtained after that sample was fired in a separate tube furnace at 1000°C for 48 hours,

indicating again that if the impure oxide is thermally stabilized, water re-adsorption can be significantly reduced.
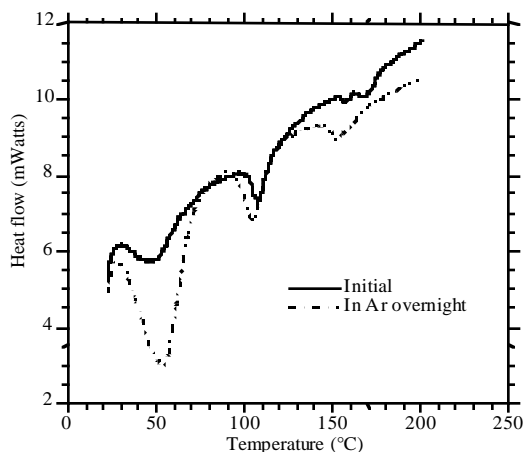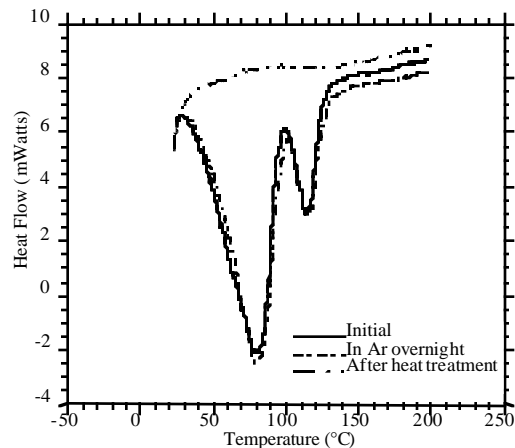
Figure 1. DTA curves for ARF365

Figure 2. DTA curves for N002a

Overall these results suggest that during storage the samples retained a small amount of water (water content of samples when originally placed in the storage containers is not given so we can not address if additional water was adsorbed during storage). The presence of $CaCl_2$ in N002a increases the amount of water initially present and the amount of water that is re-adsorbed by the sample. In addition upon exposure of the samples to water, the bulk of the water is adsorbed on the inorganic salts (and other possible contaminants) and not the plutonium oxide.

Summary

PuO_2. Plutonium dioxide contains both physically and chemically adsorbed water. For PuO_2, calcining at 700°C lowers the water content to <0.2 wt% and calcining at 950°C removes all detectable water.[3] The extent of adsorption of H_2O molecules varies widely with the kinetics of adsorption, a function of PuO_2 process history, surface area, relative humidity and time. Moseley and Wing report the coverage as high as 50 mg H_2O per g of uncalcined PuO_2 (5 wt %).[6] Haschke reports an initial monolayer of water is adsorbed at humidities less than 1%. From 1% to 20% RH, a second monolayer is adsorbed. For a sample with a surface area of 5 m^2/g or less (obtained by calcining at 950°C), two monolayer coverage corresponds to 0.18 wt% water.[3,5] Calcining at 800°C (surface area approximately 6-8 m^2/g) could raise that value to 0.26

wt% water. From 20 to 50% relative humidity no additional adsorption appears to take place. Over 50% relative humidity, additional water adsorbs at a faster rate.[3,5]

NaCl and KCl. TGA analysis of NaCl and KCl (ambient atmosphere not given) suggest, but do not confirm, all detectable water is removed by 400°C.[32] Other studies indicate NaCl and KCl can be completely dried at temperatures around 400°C, but only if heated under vacuum and/or with periodic flushing with an inert gas. When heated in air, NaCl can react with H_2O to form hydroxide (in trace amounts). This hydrolysis occurs above 850°C in a closed vessel, but at lower temperatures in an open vessel.[9] Others claim hydrolysis occurs at even lower temperatures and under very low humidity conditions: 50 layers of NaCl react at 2% relative humidity at 450°C.[14] Because the hydrolysis of NaCl and KCl to form hydroxides is primarily a surface phenomenon and the hydroxides are easily removed, the hydration of NaOH and KOH is not expected to be problematic and was not considered. NaCl and KCl will adsorb some surface water even in very low humidity environments. Full monolayer coverage of surface water occurs around 40% humidity, and deliquescence of the salt occurs at 75% and 82%, for NaCl and KCl respectively.

The drying of two mixed salt systems has been reported, 50/50 mole % KCl/NaCl and 27/35/38 mole % $NaCl/KCl/MgCl_2$.[2] Drying KCl/NaCl with Ar sparging at 740°C appears to be rigorous enough to obtain a hydroxide concentration of 0.17 mmol or 3×10^{-4} wt% expressed as water.[15] The second mixed salt ($NaCl/KCl/MgCl_2$) is not dried under these conditions, presumably due to the hygroscopic nature of $MgCl_2$. After heating the $NaCl/KCl/MgCl_2$ salt under argon above 800°C, 0.22 wt % water remains.[2]

$CaCl_2$ and $MgCl_2$. Generally, removing hydrated water from $CaCl_2$ requires heating for extended periods (for 5-7 days at 225°C) or sparging with HCl (at 850°C). Even after those treatments, the $CaCl_2$ contains 0.2-0.3 wt % water.[2] One group reports that 6.38 moles of H_2O (determined from weight loss measurements) can be removed from the dehydration of impure $CaCl_2 \cdot 6H_2O$ ($CaCl_2 \cdot 6H_2O$ with 5.1% KCl and 0.5% NaCl) at temperatures around 400°C.[18] If $CaCl_2$ is heated above 800°C in wet air it will react to form CaO and, depending on the

humidity and temperature, $Ca(OH)_2$.[16]   No information is available regarding the amount of water retained or the specific ratios of each component, $CaCl_2$, $Ca(OH)_2$, and CaO, present after heating $CaCl_2$.

One can dehydrate $MgCl_2 \cdot H_2O$ completely by heating under an HCl atmorphere at 200°C.[19] Magnesium chloride in the presence of water converts to MgO at temperatures above 505°C; but depending on the specific conditions, the conversion may not be complete. No water is detected in the $MgCl_2$ hydrolysis product, MgO, above 800°C.[4]

Complete monolayer coverage on $CaCl_2$ and $MgCl_2$ occurs at low humidity as reflected by their low deliquescence points ($CaCl_2$: 35% humidity at room temperature; $MgCl_2$: not specified). CaO and MgO will hydrate to form surface hydroxides (for MgO at humidities higher than 30%), with the extent of reaction depending on the surface area. For a series of CaO samples calcined at different temperatures, the one calcined at the lowest temperature (and hence with the largest surface area) undergoes the greatest hydration, 0.8 fractional hydration in 600 min at a partial water pressure of 2.8 kPa. Most physisorbed surface water can be easily removed; however, hydroxide removal requires more rigorous drying procedures.

Recommendations with respect to Pu stabilization (0.5 wt% H_2O criteria)

Several approaches can be chosen for stabilizing plutonium dioxide residues contaminated with chloride salts. However, unless the most critical salt present is identified and quantified, it would be prudent to assume a worst-case scenario. Plutonium dioxide itself will in all likelihood be coated with salt from the process that originally generated the residue, and in any case is less problematic with respect to moisture than the chloride salts. The alkali metal chloride salts in turn are less problematic both with respect to dehydration and rehydration than the alkaline earth chloride salts. Therefore, our recommendations are based on the assumption that calcium and/or magnesium chloride is the salt that must be processed in a manner to render the residues suitable for 3013 storage. Unfortunately, because of a lack of published scientific data regarding dehydration of salts under ambient air conditions and the effect of relative humidity and the rate of water re-adsorption for dry salts, it is difficult to unequivocally state the stabilization processing and packaging conditions required to meet the 3013 criteria.

Heating of alkaline earth chloride hydrates leads to hydrolysis, with the liberation of hydrochloric acid. Since this can both eliminate water from the residue and convert the alkaline earth chlorides to less hygroscopic oxides, the hydrolysis reaction should be encouraged. The temperature of the calcination furnace should be raised as quickly as feasible. This begs the question of what calcination temperature should be used? Literature reports indicate that heating calcium chloride to either 800 °C or 950 °C will probably dry the salt to the same extent although there is no specific account of such a process in air. However, 800 °C is only about 20 °C above the melting point of calcium chloride. Care must be taken to ensure the lowest temperature in the calcination bed is equal to or above 800°C, which would require the furnace control thermocouple to be located in the chamber. From an engineering perspective this may not be feasible. As a consequence we recommend that 850 °C be used as a minimum calcination temperature for stabilization of salt residues.

The next issue to be addressed is the amount of time required at the calcination temperature. As the salts are heated and hydrolysis occurs, hydrochloric acid will be evolved. It should be possible to determine when hydrolysis is no longer occurring, and therefore water is no longer present, by testing the process off-gas for the presence of acid gases. This could be accomplished by the simple expedient use of pH paper, although certainly more elaborate and rigorous monitoring may be used. However, if the ambient air being used for the process atmosphere has an elevated moisture content it is possible that hydrochloric acid would be continuously evolved until the chloride salt was completely hydrolyzed. This would likely be a lengthy process. Using the work of Fife with calcium chloride, an upper limit 2 hours (as currently required by the present standard) would probably be sufficient to reach equilibrium conditions between moisture initially present in the salt and the moisture content of the process atmosphere.

Another consideration exists in the use of ambient air for the process atmosphere. Magnesium chloride will react with oxygen at elevated temperatures to form magnesium oxide and chlorine. Acid-gas monitoring of the process off-gas will also indicate the presence of chlorine from this reaction. If magnesium chloride is present as a pure compound then the oxidation reaction will proceed to completion, probably in a short time. Since magnesium oxide is much less hygroscopic than magnesium chloride, this is advantageous from the perspective of

rehydration after calcination and the process should be allowed to proceed to completion. However, as is more likely the case, magnesium chloride is present along with another chloride salt with which it forms a solution, equilibrium will be reached with oxygen as the activity of magnesium chloride in the salt solution drops. Also, as the concentration of magnesium chloride falls, the kinetics of the reaction will decrease and diminishing returns will be obtained. A practical upper limit on the calcination time should be chosen. For the sake of consistency with calcium chloride, 2 hours should initially be used, although experience may prove that slightly longer times would be beneficial.

Though calcium chloride and magnesium chloride are not easily dried, the more difficult task is to maintain them in that state after calcination. It will be impossible to avoid at least a monolayer of adsorbed moisture on any of the salts unless extremely dry (ppm level) glovebox atmospheres are maintained. It is currently being proposed to carry out the calcination in pans to ensure adequate oxygenation throughout the entire depth of the container. If this is the case, we recommend covering the pans to physically limit the access of air to the oxides and salts. Haschke's work with plutonium dioxide has shown that such a physical deterrent can significantly reduce the initial rate of adsorption.[3,5] As an alternative, the best way to minimize the surface area of the salts would be to use a calcination container, such as an MgO crucible, that could be directly placed into the 3013 can. For the alkali chlorides only trace amounts of moisture would be present if this procedure is followed since the surface area of the waste would be limited to the top surface of the solidified salt pool. If the moisture level of the glovebox atmosphere was kept below critical relative humidity (~70%) then the salt could be kept in the glovebox for whatever time was convenient before being placed in a 3013 can, without picking up additional moisture.

The critical relative humidity is much lower for the alkaline earth chlorides (~35% for $CaCl_2$, value for $MgCl_2$ not given) so the moisture level in the glovebox must be maintained below this level. Even so, water can penetrate into the bulk of the alkaline earth chloride salt monolith by formation of hydrates below the critical relative humidity level. Formation of hydrates can result in large quantities of water in the salt waste. The extent to which this occurs will depend on the moisture level of the atmosphere and the length of time the salt is exposed to that atmosphere. The current standard recommends that stored sample contain less than 0.5 wt% water which could be achieved by any combination of variables. We recommend the salt residues

be sealed in 3013 containers as soon as possible after calcination (certainly within a few hours) and that some of the moisture in ambient air be removed since the 35% humidity level can be exceeded on a regular basis in some parts of the country.

Acknowledgements

References

1) "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage, "DOE-STD-3013, U.S. Department of Energy, **1996**.

2) Fife, K. W.; Bowersox, D. F.; Christensen, D. C.; Williams, J. D. "The Preparation of Fused Chloride Salts for Use in Pyrochemical Plutonium Recovery Operations at Los Alamos," Los Alamos National Laboratory, LAUR-10681, **1986**.

3) Haschke, J. M.; Ricketts, T. E. *Journal of Alloys and Compounds* **1997**, *252*, 148-156.

4) Coluccia, S.; Marchese, L.; Lavagnino, S.; Anpo, M. *Spectrochimica Acta* **1987**, *43A*, 1573-1576.

5) Haschke, J. M.; Martz, J. C. "Plutonium Storage" in R. A. Myers (Ed.): *Encyclopedia of Environmental Analysis and Remediation*, John Wiley & Sons, Inc. **1998**, pp 3740-3755.; Haschke, J. M.; Ricketts, T. E. "Plutonium Dioxide Storage: Conditions for Preparation and Handling," Los Alamos National Laboratory, LAUR-12999-MS, **1995**.

6) Stakebake, J. L. *Journal of Nuclear Materials* **1971**, *38*, 241-259.

7) Stakebake, J. L. *The Journal of Physical Chemistry* **1973**, *77*, 581-586.

8) Moseley, J. D.; Wing, R. O. "Properties of Plutonium Dioxide," The Dow Chemical Company, **1968**.

9) Gmelin, L.; *Gmelin Handbook of Inorganic Chemistry. Cl, Chlorine Supplement.* No. 6, 8th ed. Verlag Chemie: Weinhein, **1968**.

10) Gardner, H. J.; Brown, C. T.; Janz, G. J. *Journal of Physical Chemistry* **1956**, *60*, 1458-1460.

11) Barraclough, P. B.; Hall, P. G. *Surface Science* **1974**, *46*, 393-417.

12) Kaufmann, D. W. *Sodium Chloride: The production and Properties of Salt and Brine*; Hafner Publishing Company: New York, **1971**; Vol. 145.

13) Otterson, D. A. *Journal of Chemical Physics* **1960**, *33*, 227.

14) Barr, L. W.; Koffyberg, F. P.; Morrison, J. A. *Journal of Applied Physics* **1962**, *33*, 225-226.

15) Maricle, D. L.; Hume, D. N. *Journal of the Electrochemical Society* **1960**, *107*, 354-356.

16) Kondo, H.; Asaki, Z.; Kondo, Y. *Metallurgical Transactions B* **1978**, *9B*, 477-483.

17) Wenz, D. A.; Johnson, I.; Wolson, R. D. *J. Chem. Eng. Data* **1969**, *14*, 252.

18) Arbanas, V.; Bukovec, N.; Bukovec, P. *Thermochimica Acta* **1989**, *144*, 235-240.

19) Gmelin, L.; *Gmelin Handbook of Inorganic Chemistry. Mg, Magnesium, Main Volume.* No. 27, 8th ed. Verlag Chemie: Weinhein, **1968.**

20) Xia, S.; Xing, P.; Gao, S. *Thermochimica Acta* **1991**, *183*, 349-363.

21) Innes, C. J. *International Society of Leather Trader's Chemists* **1937**, *31*, 55.

22) Hucher, M.; Oberlin, A.; Hocart, R. *Bull. Soc. Fr. Mineral. Cristallogr.* **1967**, *90*, 320-332.

23) Peters, S. J.; Ewing, G. E. *Langmuir* **1997**, *13*, 6345-6348.

24) Dai, Q.; Hu, J.; Salmeron, M. *Journal of Physical Chemistry B* **1997**, *101*, 1994-1998.

25) Luna, M.; Rieutord, F.; Melman, N. A.; Dai, Q.; Salmeron, M. *Journal of Physical Chemistry A* **1998**, *102*, 6793-6800.

26) Bayh, W.; Pflug, H. *Z. Angew. Phys.* **1968**, *25*, 358-364.

27) Tang, I. N.; Munkelwitz, H. R. *Journal of Applied Meteorology* **1994**, *33*, 791-796.

28) Maciel-Camacho, A.; Hernandez, H. R.; Hills, A. W. D.; Morales, R. D. *ISIJ International* **1997**, *37*, 468-476.

29) Holt, S. A.; Jones, C. F.; Watson, G. S.; Crossley, A.; Johnston, C.; Sofield, C. J.; Myhra, S. *Thin Solid Films* **1997**, *292*, 96-102.

30) Stirniman, M. J.; Huang, C.; Smith, R. S.; Joyce, S. A.; Kay, B. D. *Journal of Chemical Physics* **1996**, *105*, 1295-1298.

31) V. Freestone, United Kingdom Aldermaston Weapons Establishment, personal communication to P. G. Eller.

32) Duval, C. *Inorganic Thermogravimetric Analysis*; Elsevier Publishing Company: New York, **1963**.

APPENDIX 1: Search methods: Database followed by keywords used.

Sci-Search
(1974-present) · **INSPEC database** · **DOE Energy database**

Sci-Search (1974-present)	INSPEC database	DOE Energy database
Sodium chloride and dehydration	Sodium chloride and water	Sodium chloride
Potassium chloride and dehydration	Potassium chloride	Potassium chloride
Magnesium chloride and dehydration	Magnesium chloride and water	Magnesium chloride
Calcium chloride and dehydration	Calcium chloride	Calcium chloride
Deliquescence	Humidity and salt	Dehydration and salt
Humidity and (plutonium oxide or magnesium oxide or calcium oxide)	Humidity and chloride	Dehydration and chloride
Desorption of water	Humidity and oxide	Dehydration and oxide
Magnesium chloride and high temperature	Dehydration and salt	Desorption and chloride
Magnesium chloride and calcination	Dehydration and chloride	Desorption and salt
Calcium chloride and high temperature	Dehydration and oxide	Desorption and water and oxide
Calcium chloride and calcination	Desorption and salt	Desorption and water and chloride
Potassium chloride and high temperature	Desorption and chloride	Desorption and water and salt
Potassium chloride and calcination	Desorption and oxide and (plutonium or magnesium)	Desorption and oxide and plutonium
Sodium chloride and high temperature	deliquescence	Desorption and oxide and magnesium
Sodium chloride and calcination		Adsorption and chloride and water
		Adsorption and salt
		Adsorption and oxide and (plutonium or magnesium)
		Relative humidity
		Humidity and salt
		Humidity and oxide
		Deliquescence

On-line Catalog	LANL Unclassified database	Sci-Finder
Sodium chloride	LOI	Hygroscopic and chloride salts
Potassium chloride	Dehydration	Deliquescence and chloride
Magnesium chloride	Humidity	Sodium chloride and relative humidity
Calcium chloride	Sodium chloride	Hygroscopic salts
Dehydration	Potassium chloride	Dehydration and sodium chloride
Humidity	Magnesium chloride	(Sodium chloride, potassium chloride, magnesium chloride or calcium chloride) and (water content)
Desorption of water	Calcium chloride	(Sodium chloride, potassium chloride, magnesium chloride or calcium chloride) and (heating or high temperature)
Adsorption of water	deliquescence	Desorption
Desorption		Skleenkova
deliquescence		Adsorption

Several discussions were also held with the scientists involved with plutonium processing.

In addition, the following books were read and were found to contain no relevant information:
1. Advances in Molten Salt Chemistry. Eds. J. Braunstein, Gleb Mamantov, and G. P. Smith; Plenum Press, New York.1971.
2. The Chemistry of Molten Salts: An Introduction to the Physical and Inorganic Chemistry of Molten Salts and Salt Vapors. Harry Bloom; W. A. Benjamin, Inc., New York. 1967.
3. Comprehensive Treatise of Electrochemistry: Vol. 5, Thermodynamic and Transport Properties of Aqueous and Molten Electrolytes. Eds. Brian E. Conway, J. O'M. Bockris, and Ernest Yeager; Plenum Press, New York. 1983.
4. Modern Aspects of Electrochemistry No. 2; Ed. J. O'M. Bockris; Academic Press Inc., New York. 1959.
5. Modern Aspects of Electrochemistry No. 9; Eds. B. E. Conway and J. O'M. Bockris; Plenum Press, New York. 1974.
6. Molten Salt Chemistry. Ed. Milton Blander; Interscience Publishers, a division of John Wiley & Sons, New York. 1964.
7. Molten Salts Handbook. George J. Janz; Academic Press, New York. 1967.
8. Physical Properties Data Compilations Relevant to Energy Storage. II. Molten Salts: Data on Single and Multi-Component Salt Systems. G. J. Janz, C. B. Allen, N. P. Bansal, R. M. Murphy, and R. P. T. Tomkins; U. S. Department of Commerce. NSRDS-NBS 61 Part II. April 1979.

APPENDIX 2. References not written in either English or German (along with translated abstracts). Also included are abstracts for articles where the journal is not available in our library.

1. "Water vapor sorption of water-soluble substances: studies of crystalline solids below their critical relative humidities." Konthy, Mark J., Grandolfi, George P., Zografi, George. Pharm. Res. (1987) 4, 104-112.

Water vapor sorption on unground and ground samples of NaCl and Na salicylate at relative humidities below Rh_o, that at which deliquescence is initiated [critical relative humidity], was measured. Sorption isotherms, expressed as the amount sorbed per unit area of solid surface, were different for unground and ground samples. Measurement of sp. Surface area for samples previously exposed to various relative humidities revealed no change with unground samples but a significant reduction with ground samples beyond about 20% relative humidity. Correcting isotherms of this change in area brings the results with ground and unground samples into closer agreement. Thus, relatively low levels of water vapor sorption on cryst. water-sol. solids, below Rh_o, can give rise to some form of surface dissolution when the solid has been subjected to various forms of mechanical disturbance.

2. "Effect of moisture in the environment on the state of the surface of articles made of alkali metal halide crystals" Skleenkova, Zh. V., Izv. Vyssh. Uchebn. Zaved., Priborostr. (1984), 27, 91-5.

The development of the thickness and n of the surface layer of NaCl and KBr crystals, used for optical instruments, was studied in relation to the relative humidity of the environment. The mechanism of H_2O sorption and the nature of the interaction of the polished surface with the adsorbed H_2O ore detd.

3. "Manufacture of granules containing sodium chloride and calcium compounds." Oyama, Toshikazu; Yasuhara, Naomi; Sudo, Yosho. Patent written in Japanese. Application JP 90-130951 900521.

The title granules are manufactured by melting >70 wt. parts NaCl and <30 wt. parts Ca compounds at 650-850 °C and spraying melted compds. The granules show less hygroscopic property than conventional NaCl crystals.

4. "Hygroscopicity of sodium chloride obtained during calcium chloride production" Zhukov, V. A.; Rusanova, T. G.; Kulagina, O. N. USSR. Deposited Doc. (1981), Issue SPSTL 43 khp-D81, 10 pp.

The rate of absorption of moisture by NaCl obtained from manuf. Of $CaCl_2$ was detd. By the dessicator method in the presence of 10, 34.8, and 46.7% H2SO4 for a corresponding relative humidity of air above H_2SO_4 of 94.3, 66.5, and 42.5%. The hygroscopic point of NaCl <45% of relative humidity and the hygroscopic mark is 9-10 (10 being the max). Thus, such a salt is unstable for storing even during dry periods of the year.

5. "Kinetics of the sorption (desorption) of water vapor on crystalline sodium chloride." Gurshkov, V. P. USSR Pishch. Promt-st. (Moscow) (1990), 8, 53-5.

Sorption desorption isotherms were detd. for cryst. NaCl (particle size 4.0 x 10-4m) at 67-82% relative humidity. The rate of sorption (desorption) of moisture depended on the initial moisture. The mechanism of sorption (desorption) of water by NaCl are discussed in relation to NaCl caking.

6. "Study of water adsorption on the surface of alkali metal halide crystals." Abaev, M. I.; Skleenkova, Zh. V. USSR. Opt.-Mekh. Prom-st. (1984) 7, 10-11

The parameters of adsorbed water layers on NaCl and KBr crystals and their changes on changing relative humidity were studied ellipsometrically. The refractive indexes (n) and the thicknesses (d) of the adsorbed layers were measured as functions of aging (time). A quasiperiodic behavior of the n and d curves vs. time was obsd.

7. "Effect of crystallographic orientation on the resistance of alkali halide crystals to moisture" Skleenkova, Zh. V.; Shilova, O. M.; Kuznetsov, S. M. USSR. Opt.-Mekh. Prom-st. (1984), 5, 24-7.

The dynamics of the surface layer water properties of KBr, KCl, and NaCl crystals was studied ellipsometrically as function of their orientation. The (100), (110), and (111) faces of the crystals were exposed to 66% humid atm. (above satd. aq. $NaNO_2$ soln). The n values of crystals changed and n = f(time) and d = f(time) behaved as quasiperiodic functions d = surface layer thickness). At the initial stage of H_2O vapor adsorption n and d changed proportionally to (time)1/2. The detd. coeffs. K (K = $(n-n_0)$/(time)1/2) and A (A = $(d-d_0)$/(time)1/2) depend on crystal orientation and reflect adsorption or desorption processes. For (100) and (111) orientation, NaCl crystals exhibits maximal and KCl minimal adsorption capacity, whereas the order is reverse for the (110) orientation.

8. "Moisture absorption processes of powder particles of some water-soluble chlorides" Kanazawa, Takafumi; Kaiho, Mamoru; Chikazawa, Masatoshi. Kogyo Kagaku Zasshi (1971), 74, 152-5. (Journal written in Japanese).

A 22-5°C and 18.30-19.95 torr H_2O vapor pressure, the moisture sorption W of NaCl, NH_4Cl, and KCl increased linearly with time. However, when the H_2O vapor pressure was neat the value corresponding to critical relative humidity, the rate of moisture sorption decreased with time, until a constant sorption rate was reached. W increased rapidly with vapor pressure. However, when the vapor pressure reached a value corresponding to the critical relative humidity the vapor pressure remained constant even in W continued to increase. Effective surface areas for sorption and film thickness are also discussed.