

*Plutonium Dioxide Storage:  
Conditions for Preparation and Handling*

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# PLUTONIUM DIOXIDE STORAGE: CONDITIONS FOR PREPARATION AND HANDLING

by

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## ABSTRACT

Desorption and adsorption properties of plutonium dioxide are derived from production-scale experiments that demonstrate techniques of preparing weapons-grade material for extended storage. In combination with relevant data extracted from literature sources, the results define conditions for preparing and certifying PuO<sub>2</sub> and provide essential information for developing and implementing a repackaging process compliant with Department of Energy standards for safe storage of plutonium. As demonstrated by results of loss-on-ignition (LOI) analysis, adsorbates are effectively removed by heating the oxide in air at 950 °C for two hours. After oxides are fired at this temperature, specific surface areas are consistently less than 5 m<sup>2</sup>/g. Due to this low surface area, water adsorption by fired oxide is limited to a maximum of 0.2 mass % at 50% relative humidity. Kinetic data for the adsorption process show that water is accommodated on the oxide surface by a sequence of distinct first-order steps comprising five types of adsorbate interaction and accumulating ten molecular layers of H<sub>2</sub>O at 100% humidity. An equation defining the humidity dependence of the adsorption rate during the first step is applied in estimating time periods that a fired oxide may remain in given configurations without detrimental adsorption. Particle size measurements show that the source terms for environmental dispersal of oxides prepared by hydride-catalyzed reaction of metal and by oxalate calcination are approximately 20 and 0.1 mass %, respectively, and that the values are reduced by firing. Evidence for a chemical reaction between dioxide and water is discussed and practical applications of the results to oxide stabilization and LOI analysis are presented.

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## INTRODUCTION

As a consequence of recent reductions in the nuclear weapons arsenal, excess weapons grade plutonium must be safely stored at DOE facilities until final disposition. A recent assessment of storage issues concludes that plutonium metal (Pu), gallium-containing alloys, and dioxide (PuO<sub>2</sub>) are suitable forms for storage of excess plutonium.<sup>1</sup> Technical issues associated with storage of these forms are identified in a DOE study that cites the need to characterize and stabilize materials prior to packaging in

sealed containers.<sup>2</sup> Although the requirements for storing metal and alloys are well established from extensive experience with weapons components, a similar knowledge base does not exist for oxide, and certain aspects of PuO<sub>2</sub> chemistry need to be defined before procedures for preparation and handling the oxide can be established.

Potential difficulties associated with oxide storage arise primarily from a combination of its chemical and physical properties.<sup>2</sup> As a consequence of high surface area and strong chemical affinity of surface sites, the dioxide can adsorb several mass percent of molecular species from the atmosphere.<sup>3-6</sup> Polar molecules such as water are strongly bound to the oxide surface.<sup>5</sup> Radiolysis<sup>2</sup> and chemical reaction<sup>7</sup> of adsorbates hold a potential for producing unacceptably high pressures of non-condensable and reactive gases during storage. For example, the amount of water present at the one-mass-percent level (10 mg H<sub>2</sub>O/g PuO<sub>2</sub>) is capable of producing a pressure of about fifty atmospheres of H<sub>2</sub> and O<sub>2</sub> in a typical storage vessel.<sup>8</sup> The hazard posed by possible rupture of an oxide storage vessel is considered to be significant because a large mass fraction of the material is thought to reside in the dispersible size range below 10 μm geometric diameter.<sup>3,9,10</sup> Additional work is needed to adequately evaluate the risk associated with pressure generation and oxide dispersal.

One requirement of the criteria for extended safe storage of plutonium dioxide is prevention of unacceptably large pressure increases in storage vessels over time.<sup>8</sup> A safe condition exists if the amount of adsorbate on the oxide is limited or if the pressurization rate is sufficiently slow that the total increase is acceptable during the anticipated storage period. The time dependence of pressure cannot be predicted because kinetic information for possible pressurization processes is unavailable. Therefore, a prudent approach has been adopted: control the maximum pressure by thermally desorbing reactive species from the oxide and restricting re-adsorption prior to sealing in the storage vessel.

As described in various reports,<sup>3, 5, 11-13</sup> adsorption and desorption data for PuO<sub>2</sub> and H<sub>2</sub>O frequently appear inconsistent, and the results are not directly applicable in resolving storage issues. For example, the extent of adsorption reported for the saturated water system at room temperature varies substantially. Whereas Stakebake and Steward measure an equilibrium loading of 0.86 mg H<sub>2</sub>O/g PuO<sub>2</sub> at room temperature and 100% relative humidity,<sup>5</sup> Moseley and Wing report saturation levels as high as of 50 mg H<sub>2</sub>O/g PuO<sub>2</sub> at those conditions.<sup>3</sup> Such discrepancies need to be addressed and data on the kinetics of adsorption are needed. The time dependence of water adsorption by dried PuO<sub>2</sub> is reported,<sup>3,11</sup> but the results do not provide an adequate technical basis for defining storage procedures.

The focus of this study is to develop information that will assist Los Alamos National Laboratory and other Department of Energy sites in establishing preparative and handling procedures needed to certify plutonium dioxide for storage. The effort has two major objectives: definition and demonstration of procedures for dioxide stabilization and correlation of data with results from literature sources. Although work in these areas is incomplete, this status report is considered appropriate because of the need for timely development of implementation plans at storage sites. The combination of experimental results from this work and information extracted from prior studies provides several conclusions that define the conditions and facilities required for implementation.

## **EXPERIMENTAL PROCEDURES**

Experiments in this study were designed to develop and demonstrate procedures for preparing and handling plutonium dioxide prior to storage while simultaneously obtaining fundamental equilibrium and kinetic information. Kilogram-sized quantities of high-purity ( $> 88$  mass % Pu) oxides were obtained from sources that might be encountered during typical re-packaging operations. In one case, the oxide (2.8 kg) had been formed by hydride-catalyzed oxidation of plutonium metal.<sup>14,15</sup> In the other case, a process oxide (2.7 kg) previously prepared by calcination of oxalate precipitate from aqueous plutonium nitrate solution was removed from storage. As-received materials were characterized prior to being fired in a series of tests at progressively increasing temperatures. After completion of selected firing steps, samples were removed for measurements of plutonium content, specific surface area, and particle size distribution. Samples were also obtained for LOI analyses to determine the residual adsorbate concentration and for experiments to measure the rates and equilibrium levels of re-adsorption in a typical air-filled glove box. Measurements with oxide obtained by calcining oxalate from aqueous plutonium chloride solution are in progress and only initial results are presented in this report. Use of the terminology "oxide from oxalate" throughout this report refers to  $\text{PuO}_2$  derived from an aqueous nitrate processing line.

During calcination, the bulk oxide was evenly distributed in a rectangular fused silica boat (18 cm  $\times$  28 cm  $\times$  8 cm deep) and heated with a resistance furnace in an air atmosphere. The firing temperature was increased in 100 °C increments from 600 to 800 °C with final calcination at 950 °C. The heating periods were 12 hours at 600 and 700 °C, 10 hours at 800 °C, and 2 hours at 950 °C

Specific surface areas and particle size distributions of the oxides were measured initially and following calcination. Surface areas were determined with a Quantachrome

Corporation Nova 1000 sorption analyzer using the BET (Braunauer-Emmett-Teller) method with N<sub>2</sub> as the adsorbate. Particle size measurements were made with a Lasentech LAB-TECH 1000 analyzer, a laser system employing the light-scattering method for size measurements up to particle dimensions of 250 μm. Deionized water was used as the suspension fluid. Mass distributions were calculated from the measured particle distributions by assuming spherical particle geometries.

Rates and equilibrium levels of adsorption during exposure of calcined oxides to air were determined by gravimetric methods. Conditions for these tests were selected to identify possible limitations on the use of air-filled glove boxes for preparing and handling oxide prior to storage at Los Alamos. The time frame of the experiments was sufficient to include seasonal fluctuations of air humidity in the plutonium facility. Experiments with the oxide formed from metal were conducted during the springtime when the relative humidity (RH) was approximately 1%; those with oxide from oxalate were made during the summer when the RH was near 10%. As shown by periodic temperature and dew-point measurements, the humidity levels remained remarkably constant during both test periods. The time dependence of adsorption was determined by measuring the mass change of an oxide sample with an analytical balance. An accurately weighed sample (approximately 50 g) of calcined oxide was spread in a watch glass and placed on the balance pan. The mass was determined at 15 minute intervals over an eight-hour period and then left for an additional fifteen hours to ensure that equilibrium had been attained. The sample was distributed over a 32 cm<sup>2</sup> area at a nominal depth of 0.6 cm. Doors to the balance chamber remained fully open at all times except when measurements were being made. In two tests with oxide formed from metal, samples were taken after calcination at 950 °C and exposed to 1% RH air for periods of 12 and 50 days, respectively, to verify that equilibrium had been reached and that other processes were not occurring.

The effect of covering the oxide during exposure to air was investigated. The adsorption rates of an oxide prepared via oxalate from chloride solution were determined for two experimental configurations. In tests at 5% RH, mass-time data were collected as described above and in parallel studies with a second watch glass inverted over the oxide sample.

Loss on ignition (LOI), the standard gravimetric procedure required for oxide certification,<sup>8</sup> was used to determine levels of residual adsorbate remaining after calcination and amounts of readsorption following air exposure. Since these analyses were performed in an analytical laboratory at a separate location from the plutonium facility, samples (2-3 g) of homogeneous (V-blended) oxide were obtained and packaged

for shipment in leak-free containers with dry argon atmospheres. The LOI analysis was made by measuring the mass lost by an accurately weighed sample (approximately 0.5 g) during a two-hour heating period at 950 °C. The oxide was contained in a platinum crucible, heated under static air in a muffle furnace, and cooled with desiccation prior to final weighing. Completeness of adsorbate removal during the LOI procedure was investigated by heating several samples to higher temperatures (1050 and 1150 °C) and for longer times (4 and 6 hours) to determine if additional mass losses occurred. The estimated uncertainty in the LOI measurements is  $\pm 0.02$  mass %.

In order to correlate findings of this study with prior results, digital data were extracted from graphical sources in several reports. Values were used only if the estimated uncertainties in the extracted quantities were less than  $\pm 10\%$ .

## RESULTS AND DISCUSSION

### Specific Surface Areas

Interpretation of the adsorption behavior of water and other molecular species on materials with large and highly variable surface areas is enhanced by knowledge of the specific surface area, SSA. Knowledge of this physical property permits meaningful quantitative comparisons of adsorption-desorption data to be made for oxides with different preparative and storage histories. Large discrepancies, such as the fifty-fold difference in equilibrium water loading cited in the Introduction, are eliminated if the quantity of adsorbate is normalized per unit of oxide surface area instead of per unit of oxide mass.

Specific areas for the two PuO<sub>2</sub> samples used in this study are listed in Table I. Initial values and those measured following calcination at temperatures between 600 and 950 °C are presented. The oxide prepared by oxalate decomposition has an area approximately three times larger than that of the oxide formed by hydride-catalyzed oxidation of plutonium metal. Although such differences in surface area are normally attributed to the formation of a finer oxide during oxalate calcination than during metal oxidation, results presented later in this report show that this conclusion is incorrect.

Significant decreases in the specific areas of plutonium oxides are induced by calcination above 600 °C. Curves in Figure 1 show the dependence of SSA values for oxides from different sources on firing temperature. Whereas data for the metal-hydride (inverted open triangles) and oxalate (open squares) products are from this study, the remaining data are from literature sources.<sup>5,11</sup> Although initial values vary by a factor of five or more, they converge rapidly over the 600 to 700 °C range and are consistently



below 5 m<sup>2</sup>/g after firing at 950 °C. Data reported by Rasmussen<sup>11</sup> for oxides with initial surface areas of 58 ± 2 m<sup>2</sup>/g show that the rates of these changes are both rapid and non-linear with calcination time. Specific areas measured after firing times of 5, 17 and 30 min at 760 °C are 10.5 ± 0.6, 7.5, and 3.4 m<sup>2</sup>/g, respectively.

Table I. Dependence of Specific Surface Area and Water Adsorption Characteristics on Oxide Source, Calcination Temperature and Relative Humidity

Calcination Temperature (°C)	Oxide from Metal-Hydride-Air		Oxide from Oxalate Calcination	
	Surface Area (m <sup>2</sup> /g)	[H <sub>2</sub> O] <sub>s</sub> at 1% RH (mg/m <sup>2</sup> )	Surface Area (m <sup>2</sup> /g)	[H <sub>2</sub> O] <sub>s</sub> at 10% RH (mg/m <sup>2</sup> )
As Received	11.3	--	29.3	--
600	10.2	--	23.9	--
700	8.1	0.17	5.7	0.24
800	7.9	--	5.8	0.095
950	4.8	0.16	2.7	0.078

### Molecular Layers

Detailed definition of adsorption and desorption processes depends on knowledge of the quantity of adsorbate in a molecular layer. Since water is the predominate adsorbate encountered during handling and storage of plutonium oxide,<sup>3,11</sup> an especially useful quantity is the mass of H<sub>2</sub>O required to cover one square meter of PuO<sub>2</sub> surface.

Derivation of the values in this report are based on conceptual models for the configuration of molecular water in a layer.

In the simplest model, the surface is covered by water molecules, each of which is assumed to occupy a definite area determined by the molecular shape and dimensions. Summation of atomic diameters for oxygen and hydrogen in the bent configuration of H<sub>2</sub>O suggests that each water molecule occupies a 4 Å × 4 Å area. As shown in Table II, 0.19 mg of H<sub>2</sub>O will form a single layer of water on each square meter of surface.

An alternative approach to defining this molecular layer is based on the association of water with specific sites on the surface of fluorite-type PuO<sub>2</sub>. Preferential cleavage of fluorite occurs parallel to the (111), (110), and to a lesser extent along the (100)

crystallographic planes. In each case, the idealized oxide surface is a 2:1 array of O and Pu atoms. Whereas each plutonium atom presumably resides in a fragment of the eight-fold cubic coordination geometry of oxygen atoms found in the bulk crystal, oxygen atoms occupy sites formed by fragments of metal tetrahedra. Without question, the strongest chemical interaction of this surface with a water molecule is the association of plutonium with the oxygen of H<sub>2</sub>O. If a molecular layer is complete when a water molecule is adsorbed on each surface metal atom, the quantity of water in that layer is defined by the concentration of Pu atoms in the surface plane. The results presented in Table II are derived for a fluorite-type structure with a cubic lattice constant of 5.398 Å for PuO<sub>2</sub>.<sup>16</sup> The calculated values do not vary significantly with crystal face and are in remarkably close agreement with the result obtained by defining the area of molecular water. Although the average result is  $0.213 \pm 0.012$  mg/m<sup>2</sup>, a value of 0.2 mg/m<sup>2</sup> is convenient for estimating the extent of molecular coverage on plutonium oxide.

Table II. Amount of Water per Molecular Layer Calculated for Different Adsorption Configurations on PuO<sub>2</sub> Surfaces

Adsorption Configuration	Molecular Area (m <sup>2</sup> /molecule)	Mass of Molecular Layer (mg/m <sup>2</sup> )
Molecular <sup>a</sup>	$16 \times 10^{-20}$	0.19
On (100) <sup>b</sup>	$14.6 \times 10^{-20}$	0.205
On (110)	$13.7 \times 10^{-20}$	0.220
On (111)	$12.6 \times 10^{-20}$	0.238

a. Molecular adsorption is based on occupancy of a 4 Å × 4 Å area by each H<sub>2</sub>O molecule.

b. Adsorption on crystallographic faces of PuO<sub>2</sub> is based on association of one H<sub>2</sub>O molecule with each surface Pu atom.

Because of differences in molecular weight, other adsorbates such as carbon dioxide might be expected to form molecular layers with mass greater than 0.2 mg/m<sup>2</sup>. For example, the mass of a CO<sub>2</sub> molecular layer is expected to be 2.4 times greater than that for H<sub>2</sub>O. However, consideration must also be given to the adsorption configuration, which determines the effective area occupied by a CO<sub>2</sub> molecule. Since a stable and probable arrangement is a bridging structure in which each CO<sub>2</sub> is bound to two adjacent Pu atoms, the area per carbon dioxide molecule is a factor of two greater than that for

water, and the mass in a monolayer of carbon dioxide is not substantially different than that for water.

## Desorption

Thermal desorption (firing) is the stabilization technique prescribed for oxide in the DOE criteria for safe storage of surplus plutonium,<sup>8</sup> but processing conditions such as temperature and time are not specified. Storable oxide is required to have a residual adsorbate level less than 0.5 mass % as determined by LOI analysis. Quantitative desorption data are needed to facilitate selection of process conditions and equipment for achieving the desired LOI. Complications arise because of uncertainties about changes in the oxide over time. Rapid adsorption of water occurs after calcined oxide is exposed to air, but desorption studies of oxides exposed to air for periods of weeks or years show that off-gases include CO, CO<sub>2</sub>, and NO<sub>x</sub>, in addition to H<sub>2</sub>O.<sup>4,6</sup> These observations suggest that the adsorbates present on oxide stored in air change over time to include carbonates and nitrates or chemisorbed nitrogen oxides formed by radiolysis of air. These observations lead to questions about possible differences in the desorption characteristics of oxides with different storage histories.

Literature results of desorption studies are reported for oxide after calcination and exposure to water vapor<sup>5</sup> and after extended storage in air.<sup>4</sup> These data, which were obtained by microbalance methods, are compared in Figure 2. Specific areas are reported for the oxides used in those studies, and adsorbate levels are quantified in units of milligrams per square meter. Physisorbed species removed below 50 °C are excluded from the data sets. Data points in Figure 2 indicate the stable conditions attained following incremental increases in temperature from 50 to 1000 °C. Results for oxides exposed to saturated water vapor at 27 °C and to air for five years are indicated by open and solid symbols, respectively. In each case, the concentration of adsorbate remaining at 50 °C is approximately 0.6 mg/m<sup>2</sup>, or three molecular layers of adsorbate.

A three-step desorption process is suggested by the curve for oxide exposed to water vapor. The first step, corresponding to the loss of approximately one molecular layer (0.2 mg/m<sup>2</sup>), is observed between 50 and 225 °C. The mass lost upon heating to 500 °C corresponds roughly to desorption of a second molecular layer. Removal of the final tenaciously held layer is apparently complete by 950 °C, but the precise temperature dependence of the residual water concentration remains rather uncertain due to the absence of data for 900 °C

The desorption curve for air-exposed oxide in Figure 2 corresponds well with that for water-exposed oxide at temperatures below 400 °C. The data, which are averaged

values of duplicate measurements, differ noticeably from the results for water at temperatures above 600 °C. Approximately 1.5 molecular layers (0.3 mg/m<sup>2</sup>) are apparently lost during heating to 400 °C. A step corresponding to desorption of an additional molecular layer appears between 500 and 650 °C. In a final step similar to removal of the tenaciously bound water, the remaining half-layer is desorbed by heating above 900 °C.

Interpretation of the desorption process is aided by mass spectrometric analysis of gaseous products formed during dynamic outgassing of stoichiometric PuO<sub>2</sub>.<sup>4</sup> By a factor of five to ten, water is the predominant gaseous product at temperatures up to 450 °C, but the amount of H<sub>2</sub>O formed at 500 to 600 °C is only half that of CO and of CO<sub>2</sub>. The close agreement between the curves in the low temperature region of Figure 2 also suggest that water is the primary off-gas product during the first desorption step of air-exposed oxide. Divergence of the curves above 400 °C suggests that some species other than water is desorbed from air-exposed oxide in the 500 to 650 °C range. The distinct desorption step at these temperatures is attributed to decomposition of carbonate or other chemisorbed forms of CO<sub>2</sub>. The gradual desorption occurring above 650 °C closely parallels the behavior observed for water desorption at these temperatures and suggests that a fractional layer of tenaciously bound H<sub>2</sub>O remains until the oxide is heated above 900 °C.

The results of desorption measurements conducted in this study are consistent with reports in the literature. The mass percentages and corresponding surface concentrations of adsorbate remaining after firing of air-exposed oxides are presented on Table III. The LOI results for oxide from metal are in excellent agreement with the desorption curve for air-exposed oxide in Figure 2. For example, the residual surface concentration of 0.03 mg/m<sup>2</sup> measured after firing at 800 °C<sup>4</sup> is in excellent agreement with the value of 0.04 mg/m<sup>2</sup> obtained in this study. However, the apparent surface concentrations of adsorbate remaining after firing oxide from oxalate at 700 and 800 °C are several times higher than those for oxide from metal. A possible explanation for this discrepancy is discussed in the section on Particle Size Distributions.

The effectiveness of firing oxide in air to meet or exceed LOI requirements for storage is demonstrated by the results of tests with kilogram-size quantities of PuO<sub>2</sub>. Results for both oxides used in this study show that desorption is complete at 950 °C. LOI data for oxide from aqueous chloride solution fired at 980 °C show small ignition losses on the order of the analytical uncertainty ( $\pm 0.02$  mass %). Confidence in the LOI results is high because neither increasing the temperature nor extending the heating period during analysis resulted in additional desorption.

Table III. Loss on Ignition Results for Oxides Calcined at Different Temperatures

Calcination Temperature (° C)	Loss on Ignition (LOI) Results			
	Oxide from Metal-Hydride-Air (mass %) (mg/m <sup>2</sup> ) <sup>a</sup>		Oxide from Oxalate Calcination (mass %) (mg/m <sup>2</sup> ) <sup>a</sup>	
As Received	0.52	0.46	0.97	0.33
600	0.16	0.16	0.57	0.24
700	0.05	0.06	0.09	0.16
800	0.03	0.04	0.14	0.24 <sup>b</sup>
950	0.00	0.00	0.00	0.00

- a. Values of mg/m<sup>2</sup> were calculated from mass percentages using specific surface areas in Table I.  
 b. The anomalous result at 800 °C is attributed to an error arising from exposure to moisture during handling or from inaccurate LOI analysis.

### Adsorption

An adequate understanding of water re-adsorption by the fired oxide prior to sealing of the storage container is essential for identifying conditions, equipment and procedures needed to maintain a desired LOI during handling operations. Two aspects of the adsorption process are relevant. One area of relevance is the relationship between conditions and the equilibrium or, saturation level of adsorption. The other area is the relationship between conditions and the rate of adsorption. Although the adsorption behavior of PuO<sub>2</sub> is described in several reports,<sup>3,5,11,12</sup> the adsorption process is inadequately understood for addressing either equilibrium or kinetic behavior of the oxide.

Time Dependence of Adsorption. Water is the primary adsorbate of interest during handling of stabilized plutonium oxide. Adsorption of carbon dioxide and nitrogen oxides is considered insignificant during the time period (< 1 day) anticipated for the packaging process. The absence of adsorbates other than water is suggested by the excellent agreement observed between results obtained in air as part of the present study and those obtained from measurements in which oxide was exposed only to high-purity water vapor.

Equilibrium and kinetic data for the adsorption process of water are both derived from the time dependence of mass during exposure of the oxide to a humid environment. As shown by Figure 3, the mass gain by fired PuO<sub>2</sub> in constant-humidity air increases at a progressively decreasing rate until a stable equilibrium, or saturated condition, is

reached. Open and solid symbols define the behavior of oxide from metal after firing at 700 and 950 °C, respectively. Results of extended tests show that the equilibrium value is invariant over several weeks at constant temperature and humidity. Although a two-fold decrease in the affinity of oxide for water apparently occurs when the firing temperature is increased from 700 to 950 °C, the observed decrease in adsorbate loading after heating at the higher temperature is due to the reduction in oxide surface area. Data in Table I show that the concentration of water per unit surface area at saturation,  $[H_2O]_s$ , is essentially equal (0.17 versus 0.16 mg/m<sup>2</sup>) and imply that the oxide surface is comparably clean and active after firing at the two temperatures. This observation conflicts with LOI results (see Table III) indicating that approximately 30% of a molecular layer of water (0.06 mg/m<sup>2</sup>) remains after firing at 700 °C. If this amount of water were present on the oxide surface after firing, the observed  $[H_2O]_s$  value would not exceed 0.10 mg/m<sup>2</sup>. This discrepancy is addressed in the section on Particle Size Distributions.

Adsorption data measured for oxide prepared by calcining oxalate from chloride solution are not consistent with those for oxides from metal and aqueous nitrate solution. The initial adsorption rate at 5% RH is a factor of fifteen slower than that for oxide from metal at 1% RH and a factor of fifty slower than for oxide from nitrate solution at 10% RH. The adsorption process for oxide from aqueous chloride is erratic, and equilibrium is apparently not attained even after several days in air.

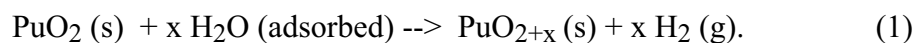
Equilibrium Behavior. Dependence of the equilibrium water concentration for plutonium oxide,  $[H_2O]_s$ , on humidity at room temperature ( $23 \pm 2$  °C) is shown by Figure 4. The data, which include values from literature sources<sup>5,11,12</sup> and from Table I, form two distinct sets based on the firing history of the PuO<sub>2</sub>. The oxides used in measuring the lower group of curves were prepared by heating in vacuum at 100 °C<sup>12</sup> (open circles) or by "drying to constant weight" (open and solid upright triangles and solid squares).<sup>11</sup> In analytical procedures, the quoted terminology is commonly used to describe heating of a material to constant mass in air at 100 °C. The oxide used in measuring the upper curve was fired at 900 °C (solid circles).<sup>5</sup>  $[H_2O]_s$  values for oxide from metal and from oxalate in Table I are shown in Figure 4 by open squares and open inverted triangles, respectively. Each data point defines the stable  $[H_2O]_s$  observed after equilibration of the oxide at the indicated water concentration.

The shapes and magnitudes of the curves in Figure 4 are important for determining conditions that effectively limit adsorption of water by fired oxide during handling. In both data sets, the  $[H_2O]_s$  values rise sharply at low moisture levels, but then remain relatively constant until the relative humidity exceeds 50%. The segments of essentially

constant  $[\text{H}_2\text{O}]_s$  correspond to the adsorption of approximately one molecular layer ( $0.2 \text{ mg/m}^2$ ) by oxide dried at  $100 \text{ }^\circ\text{C}$  and to about two molecular layers ( $0.4 \text{ mg/m}^2$ ) by oxide fired at  $900 \text{ }^\circ\text{C}$ . These observations suggest that approximately one monolayer of water remains on the oxide after heating at  $100 \text{ }^\circ\text{C}$ . Consequently, exposure of oxides to atmospheres with RH values up to 50% ( $\sim 15,500 \text{ ppm H}_2\text{O}$ ) apparently results in a total adsorbate loading of approximately two molecular layers regardless of whether the oxide is dried at  $100 \text{ }^\circ\text{C}$  or fired at a higher temperature. The adsorption of one monolayer by dried oxide at humidities below 1% RH may follow a Langmuir isotherm, but the data are insufficient to assess the behavior.

A significant inconsistency appears between the residual adsorbate level defined for  $100 \text{ }^\circ\text{C}$  in Figure 2 and that implied by interpretation of Figure 4. Whereas approximately 2.5 molecular layers ( $0.5 \text{ mg H}_2\text{O/m}^2$ ) apparently remain after the oxide is dried (Figure 2), the adsorption results suggest that about  $0.2 \text{ mg H}_2\text{O/m}^2$  remains after heating at  $100 \text{ }^\circ\text{C}$  (Figure 4). The discrepancy of about 1.5 molecular layers is diminished somewhat if a fraction of an adsorbate layer is retained on the oxide after firing at  $900 \text{ }^\circ\text{C}$ , a possibility enhanced by appropriate interpolation of the water desorption curve in Figure 2. However, this effect can account for only about 25% of the difference.

The discrepancy of about 1.5 molecular layers most likely arises because of chemical reaction involving adsorbed water and the dioxide. Although desorption is the only mechanism generally considered to be operative during thermal treatment, adsorbed water may also be eliminated by Equation (1), a process that occurs with negligible mass loss:



This reaction involves a mass loss equal to 11% of water desorption, is rapid at  $250 \text{ }^\circ\text{C}$ ,<sup>7</sup> and proceeds at a measurable rate over a wide temperature range. Occurrence of the process described by Equation (1) at room temperature is evidenced by continuous formation of pure hydrogen by water-saturated oxide at a rate of approximately  $3.2 \pm 1.3 \text{ nmol H}_2/\text{m}^2 \text{ day}$ .<sup>17</sup> As discussed in a recent report,<sup>7</sup> reaction of adsorbed water during drying is indicated by a recurring irreversibility in which the oxide mass progressively increases after each cycle of water saturation at  $27 \text{ }^\circ\text{C}$  and heating to constant mass at  $100 \text{ }^\circ\text{C}$ .<sup>12</sup> The average mass increase during five repetitive cycles ( $1.4 \text{ mg/g cycle}$ ) corresponds to the reaction of about 0.5 molecular layers of water during each cycle. Although a quantitative estimate cannot be made because heating times are not reported, several results support the possibility that adsorbed water is removed by chemical

reaction at 100 °C according to Equation (1), and that only one monolayer of water remains on the oxide surface after drying at that temperature.

An unexplained decrease in  $[\text{H}_2\text{O}]_s$  is observed for the oxide from oxalate during the adsorption studies at 10% RH. As shown by the data in Table I and the inverted open triangles in Figure 4, the equilibrium loading after firing the oxide at 700 °C lies on the upper adsorption curve for high-fired oxide. However, the  $[\text{H}_2\text{O}]_s$  values after heating at 800 and 950 °C lie on the lower curve for dried oxide. Although additional work is needed to verify and understand this behavior, its occurrence does not alter any of the conclusions drawn in this report.

Kinetic Behavior. The kinetics of water adsorption by plutonium oxide are complex. As established by earlier workers,<sup>3</sup> the adsorption rate (R) is a function of specific surface area (SSA), relative humidity (RH), and time (t), but also depends on the process history of the oxide. The shapes of the time-dependent portions of the adsorption curves in Figure 3 suggest an exponential relationship characteristic of a first-order process. As shown by kinetic evaluation of those data in Figure 5, the appearance of linear regions in the  $\ln R$ -t curves for oxide fired at 700 °C (open circles) and at 950 °C (solid circles) are consistent with this assessment. However, in both cases, the rates observed initially are noticeably slower than those predicted by extrapolation of the linear segments to zero time.

Kinetic results presented in Figure 5 provide insight into the adsorption process for water. The appearance of linear segments at  $t > 0.50$  and  $> 0.75$  hr for oxide fired at 950 and 700 °C, respectively, implies that water adsorption is a first-order process occurring after an initial adsorption step is complete. In the linear region, R is determined apparently by the concentration of equivalent adsorption sites remaining on the surface at each point in time. First-order rate constants defined by the slopes of the linear segments are presented in Table IV. At 1% RH, the average value of  $k_1$ , the rate constant for adsorption of the initial first-order process, is  $-2.3 \pm 1.0 \text{ hr}^{-1}$ . A dependence of R on the firing temperature of the oxide may exist, but the data are insufficient to evaluate that possibility.

The initial process of water adsorption on plutonium oxide is apparently not first order. The absence of first-order behavior is evident because the measured rates lie below the line defined by extrapolation of the first-order segment to lower times. The concentration of water achieved during the initial step is  $0.111 \text{ mg/m}^2$  for oxide fired at 700 °C and  $0.119 \text{ mg/m}^2$  for oxide fired at 950 °C. These values equal half the amount of water ( $0.22 \pm 0.01 \text{ mg/m}^2$ ) required to form one molecular layer on common crystallographic faces of  $\text{PuO}_2$ . Appearance of kinetic changes at these reproducible



points suggest that water adsorption is a stepwise process in which a new step begins only after the preceding step is complete for the entire oxide sample.

Table IV. Kinetic and Equilibrium Results for Adsorption of Water by PuO<sub>2</sub> as a Function of Process History and Humidity

Oxide Source	Calcination Temperature (°C)	RH <sup>a</sup> (%)	Specific Area (m <sup>2</sup> /g)	[H <sub>2</sub> O] <sub>s</sub> (mg/m <sup>2</sup> )	First-Order Rate Constant (hr <sup>-1</sup> )			R <sub>0</sub> (mg/m <sup>2</sup> hr)
					k <sub>1</sub>	k <sub>n</sub>	k <sub>n+1</sub>	
					Metal	700	1	
Metal	950	1	4.8	0.16	-3.27	--	--	0.37
Oxalate	700	10	5.7	0.23	-4.14	-0.44 <sup>b</sup>	--	0.52
Oxalate <sup>c</sup>	350	76	57	0.31	--	-0.36 <sup>d</sup>	-0.27	0.10
Peroxide <sup>e</sup>	-- <sup>f</sup>	98±2	20	1.8	--	-0.55	-0.55	0.78

- Relative humidity values are for temperatures in the range 23 ± 2 °C.
- In this case, n = 2, corresponding to adsorption of the second layer of molecular water.
- Data are from Reference 11.
- The value of n is ≥ 2; the oxide was prepared by calcination of oxalate at 350 °C and was apparently dried at 100 °C prior to the adsorption test.
- Data are from Reference 3.
- The oxide was dried in a stream of air (RH ≤ 5%) at room temperature before the adsorption test.

Additional insight into the initial adsorption process is gained by evaluation of data for oxide prepared from oxalate. The first-order analysis in Figure 6 is derived from the mass-time curve for adsorption after firing the oxide at 700 °C and exposing the product to 10% RH air. The results closely parallel those for 1% RH in Figure 5. The change from the initial adsorption process to the first-order step after about 0.3 hr is extremely sharp and again corresponds to adsorption of 0.11 mg/m<sup>2</sup> of H<sub>2</sub>O. Increasing the RH from 1% to 10% sufficiently extends [H<sub>2</sub>O]<sub>s</sub> that the second adsorption step is completed and a third step is entered after 1.2 hr. The total surface concentration of water (0.22 mg/m<sup>2</sup>) at the point of entry into the third adsorption step coincides precisely with one molecular layer and shows that the second adsorption step is also a half-layer process. The results in Table IV show that the kinetic constants depend on atmospheric water concentration. R<sub>0</sub>, the adsorption rate at zero time, increases from an average value of 0.31 ± 0.06 mg/m<sup>2</sup> hr at 1% RH to 0.52 mg/m<sup>2</sup> hr at 10% RH. A similar change in k<sub>1</sub> from -2.3 hr<sup>-1</sup> to -4.1 hr<sup>-1</sup> is also induced by the ten-fold increase in humidity. If the

third step is assumed to be first order, the rate constant,  $k_2$ , is a factor of ten smaller than that for step two.

Stepwise water adsorption is also shown by evaluation of kinetic data from the literature. A first-order analysis of rates extracted from the mass-time curve reported by Rasmussen<sup>11</sup> is presented in Figure 7. As shown in Table IV, the oxide used in this measurement was prepared from oxalate and "dried" before being exposed to a controlled 76% RH atmosphere at room temperature. If the preceding assessment of desorption behavior is correct, the first and second steps with a combined surface concentration equivalent to one molecular layer of water should not be observed during these measurements.

The  $\ln R$ - $t$  data in Figure 7 are consistent with the anticipated behavior. Evidence is not found for either the initial step or the subsequent first-order step. The first adsorption process seen in the analysis is first order, involves one molecular layer of water, and has a rate constant ( $k_n = -0.36 \text{ hr}^{-1}$ ) similar to  $k_2$  ( $-0.44 \text{ hr}^{-1}$ ) obtained from Figure 6. Although the adsorption results for dried oxide in Figure 4 suggest that  $n = 2$ , the step cannot be precisely identified. A second first-order step occurring at a slightly slower rate ( $k_{n+1} = -0.27 \text{ hr}^{-1}$ ) is entered after the surface concentration exceeds  $0.2 \text{ mg/m}^2$ . In comparison with results of similar measurements, the kinetic results presented for 76% RH in Table IV are consistently lower than those obtained for 10% RH in this study. However, the equilibrium concentration at 76% RH ( $[\text{H}_2\text{O}]_s = 0.31 \text{ mg/m}^2$ ) is in excellent agreement with equilibrium adsorption data for dried oxides in Figure 4. These results suggest that the kinetics were altered by an experimental configuration that slowed the adsorption rate, but did not decrease the ultimate extent of adsorption.

Kinetic results in Figure 8 show the behavior of oxide in  $98 \pm 2\%$  relative humidity air at  $22 \text{ }^\circ\text{C}$  after the material had been dried at room temperature in a stream of air with less than 5% RH.<sup>3</sup> The experimental mass-time data indicate that the equilibrium condition had not been reached when the measurement was terminated after a twenty-four-hour period. Although the amount of water remaining on the oxide surface after the drying step is unknown, data for 1% RH in Figure 4 suggest that the equivalent of one molecular layer of water was present initially. If that layer is included, the saturated water loading at room temperature is approximately ten molecular layers. The  $\ln R$ - $t$  curve shows three well-defined regions which apparently correspond to different types of adsorption processes. The presence of at least one molecular layer prior to the measurement is confirmed by the absence of the rapid initial adsorption steps seen in Figures 5 and 6.

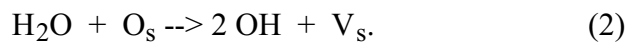
As anticipated, the first-order rate constants depend on humidity and on the extent of adsorption. The first-order rate constants measured at 98% RH are consistent with the trend established by  $k$  values for 1 and 10% RH in Table IV. As indicated by the average first-order rate constant ( $k_n$  through  $k_{n+5} = -0.55 \text{ hr}^{-1}$ ) defined by the initial slope in Figure 8, the kinetic behavior of the first six molecular layers ( $1.2 \text{ mg/m}^2$ ) is similar to the processes defined by  $k_2$  and  $k_n$  in Figures 6 and 7, respectively. Resolution of the individual steps within the group is apparently precluded by the normalizing effect of high water concentration and by absence of the necessary sensitivity in the mass-time data. The first-order rate constant ( $k_{n+6}$  and  $k_{n+7} = -0.23 \text{ hr}^{-1}$ ) for the second linear region defines the behavior of two additional molecular layers. The two-fold change observed in the rate constant suggests that attractive forces are lower than for the preceding region. A second two-fold change in the first-order constant ( $k_{n+8} = -0.12 \text{ hr}^{-1}$ ) appears upon entry into the third region and suggests that the final layer is weakly bound to the surface. This outer layer was approximately 80% complete when the measurements were terminated.

Five distinctly different types of interaction are indicated for the adsorption of water on the surface of plutonium oxide at room temperature. As demonstrated by the kinetic data in Figures 5 through 8, the types of processes and the total number of steps observed in attaining an equilibrium configuration depend on surface condition and humidity as well as temperature. Except for the first process, all individual steps are first order with rates at constant humidity apparently determined by the concentration of vacant sites in the molecular layer being occupied. Definition of the physicochemical processes occurring for each type of adsorption is aided by examining the strengths of possible surface interactions. A simple approach employing thermodynamic data for water<sup>18</sup> and for compounds of plutonium with oxygen<sup>19</sup> and hydrogen<sup>20</sup> shows that Pu-O interactions are significantly stronger than Pu-H or O-H interactions. Consequently, the initial step is expected to involve association of oxygen with plutonium atoms at the air-oxide interface.

Kinetic results for the initial adsorption implies that the process is unique to a clean or fully desorbed oxide surface. That process consumes one-half molecular layer of water and occurs in a precisely defined step consistent with the absence of time-dependent adsorbate rearrangement anticipated for a surface having a range of essentially equivalent adsorption sites. The initial process is attributed to strong interaction of an oxygen-containing species such as  $\text{H}_2\text{O}$ ,  $\text{OH}$ , or  $\text{O}$  with plutonium. As shown in Table II, association of one  $\text{H}_2\text{O}$  with each surface atom of plutonium is physically possible, but corresponds to adsorption of one water layer, not to a half layer. In addition, the  $\text{H}_2\text{O}$ -Pu

interaction is not the most energetically favorable chemical arrangement. Adsorption of atomic oxygen requires complete dissociation of water and occupation of sites formed by fragments of metal octahedra. The process does not accommodate hydrogen and is expected to involve one molecular layer of water since equal numbers of octahedral sites and plutonium atoms exist in the fluorite structure of PuO<sub>2</sub>. Furthermore, the net result of oxygen adsorption is described by Equation (1), a reaction that is known to be extremely slow compared to the initial adsorption process.<sup>18</sup>

Only one process, the dissociative adsorption of water as OH, satisfies all features of the first adsorption step. That process involves reaction of water with surface oxygen (O<sub>s</sub>) according to Equation (2):



In addition to two hydroxyl groups, a vacancy (V<sub>s</sub>) is formed by removing oxygen from a tetrahedral-fragment site at the oxide surface. Each OH formed by the process associates with a surface plutonium atom, and only one-half molecular layer of water fully covers the oxide surface. Although the mechanism of this process is unknown, possible steps are consistent with a rapid rate; ample oxygen is available at the surface, and collision of H<sub>2</sub>O with the surface should have a reasonable probability of forming product.

The second adsorption step is also attributed to dissociative reaction of water. Like the first step, this process involves one-half molecular layer of H<sub>2</sub>O, but the kinetics are apparently first-order. Since the highly active plutonium sites are fully occupied during the first step, adsorption should occur at the next most energetically favorable site, the vacancy created during the initial step. In this process, each water reacts with a surface oxygen according to Equation (2), and the resulting hydroxyl groups occupy V<sub>s</sub> sites formed concurrently and during the first adsorption step. The difference in kinetic behavior of the first and second steps may arise because of energetic constraints. Reaction of H<sub>2</sub>O with Pu during the initial step probably provides enough energy to drive the entire process, but interaction of water with V<sub>s</sub> may have insufficient energy unless the process occurs in concert with occupation of a preexisting vacancy. Spectroscopic measurements during adsorption might be used effectively to verify the chemistry and clarify mechanistic features of both the first and second adsorption steps.

The remaining three types of water association with plutonium oxide apparently involve adsorption of molecular water on the PuO(OH)<sub>2</sub> surface formed by completion of the first and second steps. As shown by Figure 7, adsorption seems to occur in monolayer steps of 0.2 mg/m<sup>2</sup>, but the kinetic differences between those steps are small, especially at high humidity. Whereas the third type of adsorption shown by Figure 8 involves six molecular layers that are apparently held by strong physisorption, the fourth

process involving two molecular layers is attributed to weak physisorption. The fifth process is thought to closely resemble condensation of water on the surface.

A quantitative description the water adsorption rate is derived for the initial step. Except for the result at 76% RH, values of the zero-time rate ( $R_0$ ) listed in Table IV suggest a regular dependence of adsorption rate on atmospheric water concentration. Definition of an average linear rate ( $R_L$ ) is convenient for determining how rapidly the adsorption front advances from the air-solid interface into the oxide.  $R_L$  values (1.0 and 2.0 cm/hr) for 1 and 10% RH are based on the respective time periods ( $0.6 \pm 0.1$  and 0.3 hr) required to penetrate the 0.6-cm-deep oxide samples ( $2 \text{ g/cm}^3$  bulk density) used in adsorption tests. An  $R_L$  value at 100% RH (3 cm/hr) was estimated to be three times that for 1% RH on the basis of the data for  $R_0$  in Table IV. The humidity dependence of  $R_L$  in units of centimeters per hour is defined by Equations (3) and (4):

$$R_L \text{ (cm/hr)} = 1.0 + \log_{10} (\text{RH in \%}). \quad (3)$$

$$R_L \text{ (cm/hr)} = -3.0 + \ln (\text{H}_2\text{O concentration in ppm}). \quad (4)$$

The rate of the initial adsorption process is substantially reduced by physically limiting access of air to the oxide. In two tests, placement of a cover over the oxide reduced the rate of water adsorption by factors of eight and sixteen, respectively.

### Particle Size Distributions

As noted in the Introduction, the potential hazard of oxide dispersal is of concern. Process oxides prepared by calcination of oxalate are thought to present a particularly serious hazard,<sup>2,10</sup> but this conclusion is not supported experimentally because particle size data are not reported. Size measurements for the product from air oxidation of metal at room temperature show that 97 to 100% of the particles have geometric diameters less than  $5 \mu\text{m}$ .<sup>6,21</sup> Since specific surface areas and particle dimensions are inversely correlated, SSA data for process oxides have been used as indicators of size distribution.<sup>2</sup> Relative to the specific areas of 5 to  $15 \text{ m}^2/\text{g}$  shown for oxides from metal in Figure 1, SSA values for process oxides from calcination of oxalate, peroxide, and hydroxide are in the 25 to  $60 \text{ m}^2/\text{g}$  range. Consequently, these process oxides have been assumed to have dispersal source terms of 100 mass %. Size distributions determined as part of this study provide essential data as well as insight into the effect of thermal processing on those distributions.

Results of particle size measurements on oxides from metal-hydride and oxalate sources in Table V show that the assumed correlation of SSA and particle size is invalid. The cumulative mass fraction of particles  $\leq 10 \mu\text{m}$  diameter for the oxide from metal-hydride is in excellent agreement with that obtained for controlled oxidation of

hydride.<sup>22,23</sup> However, the corresponding value for as-received oxide from oxalate (0.1 mass %) is a thousand-fold lower than expected.

Table V. Size Distribution Data for PuO<sub>2</sub> from Metal-Hydride and Oxalate Sources before and after the Calcination Cycle<sup>a</sup>

Particle Diameter ( $\mu\text{m}$ )	Oxide from Metal-Hydride-Air			Oxide from Oxalate		
	Mass Fraction <sup>b</sup>		Sintering <sup>c</sup> Factor	Mass Fraction <sup>b</sup>		Sintering <sup>c</sup> Factor
	As Received	Calcined		As Received	Calcined	
3	$6.1 \times 10^{-3}$	$4.5 \times 10^{-4}$	13.5	$2.2 \times 10^{-5}$	$7.3 \times 10^{-6}$	3.0
5	0.029	$2.4 \times 10^{-3}$	12.1	$1.3 \times 10^{-4}$	$4.3 \times 10^{-5}$	3.0
10	0.17	0.021	8.1	$1.3 \times 10^{-3}$	$4.5 \times 10^{-4}$	2.9
20	0.56	0.13	4.3	0.011	$3.6 \times 10^{-3}$	3.2
30	0.83	0.33	2.5	0.039	0.014	2.8

- The 36-hour calcination cycle consisted of twelve-hour heating periods at 600 and 700 °C, a ten-hour period at 800 °C, and a two-hour period at 950 °C.
- Mass fractions are cumulative.
- The sintering factor is the ratio of the as-received mass fraction to the calcined mass fraction.

Reductions in dispersible mass fractions as a result of firing the oxide are indicated by results of sintering factors, the ratio of as-received mass fraction in a size range to the mass fraction in that range after firing. As shown in Table V, the effect is most pronounced for the finely divided product from metal-hydride. The mass fraction in the respirable range below 3  $\mu\text{m}$  particle diameter is reduced by a factor of thirteen after the thirty-six-hour firing process; the dispersible fraction is reduced by a factor of eight. In contrast, sintering factors for oxide from oxalate are approximately three for all mass fractions up to 30  $\mu\text{m}$  diameter.

Certain properties relevant to adsorption and desorption depend strongly on the source and processing history of the oxide. Whereas the substantial sintering factors presented for oxide from metal in Table V are accompanied by a modest decrease in SSA, the comparatively small factors for oxide from oxalate are accompanied by large decreases in SSA. This difference in behavior apparently arises because oxide from oxalate is highly porous.<sup>11</sup> Data presented by Rasmussen show that surface area and porosity have a parallel dependence on firing time at 760 °C. Therefore, the large SSA

decrease observed in Figure 1 for oxide from oxalate arises primarily from loss of porosity during firing.

Anomalies observed in the area-normalized LIO results for oxides from metal and oxalate are attributed to porosity effects. Results in Table III show that substantial amounts of adsorbate remain after the oxides are fired at 600 to 800 °C. However, adsorption data show that the equilibrium concentrations and stepwise kinetics of the oxides fired at 700 °C are indistinguishable from those observed after the oxide is fired to zero LOI at 950 °C. Sharp decreases in SSA values of the oxalate products occur within a matter of minutes at 600 to 800 °C and are attributed to rapid closure of porosity channels in the oxide at those temperatures.<sup>11</sup> That process can easily trap adsorbed water in closed channels of the oxalate product and gives rise to an LOI value (0.16%) corresponding to about one molecular layer of surface water after firing at 700 °C. Observation of a lower LOI value (0.05%) after firing oxide from metal at that temperature suggests that its porosity and tendency to trap water are comparatively low. This interpretation of the relationship between porosity and LOI accounts for the presence of residual adsorbate even though the equilibrium and kinetic results in Table I and in Figures 5 and 6 indicate that oxide surfaces are water-free after firing at 700 °C. Consequently, the mass percentages determined by LOI analysis after firing are attributed to residues occluded in the oxide.

## **Applications**

Results of this study provide relevant information that defines conditions and requirements for preparing, protecting, sampling, and certifying plutonium dioxide prior to extended storage in sealed containers. In this section, an attempt is made to apply those results in defining conditions required for adsorbate removal, for prevention of re-adsorption and, for reliable LOI analysis.

Desorption Conditions. Firing in air at 950 °C for two hours effectively removes adsorbates (LOI = 0.00%) from kilogram quantities of plutonium dioxide powder distributed in a container at a nominal depth of 2.5 cm. Water, carbonates, and other species present after extended exposure of the oxide to air are eliminated. The residual adsorbate levels observed after firing at 600 to 800 °C varies with temperature and source (preparative history) of the oxide. The level of residual adsorbate retained by highly porous oxide from oxalate is greater than that retained by oxide from metal and may exceed 0.5 mass % after firing at 600 to 700 °C.

Adsorption Maxima. At a given temperature, the maximum (equilibrium) amount of water adsorbed by plutonium dioxide after firing depends primarily on the firing

temperature and to a much lesser extent on atmospheric water concentration. The firing temperature determines the specific surface area, which is consistently less than 5 m<sup>2</sup>/g for oxide heated above 800 °C. At room temperature and 1 to 50% RH (310 to 15,500 ppm), the corresponding equilibrium adsorbate loading is 0.2 to 0.4 mg H<sub>2</sub>O/m<sup>2</sup>. Consequently, if oxide fired at 950 °C (SSA ≤ 5 m<sup>2</sup>/g) remains in 50% RH air for an extended period, it is expected to adsorb a maximum of 0.2 mass % of water. In air with 310 ppm of water, the maximum is 0.1 mass % at equilibrium.

The importance of firing temperature and specific surface area in determining the maximum level of adsorption is demonstrated by results for oxide from oxalate fired at 600 °C. After the product is heated at that temperature, relatively high values are observed for both the residual adsorbate level (0.57 mass %) and the SSA (23.9 m<sup>2</sup>/g). In 10% RH air where [H<sub>2</sub>O]<sub>s</sub> is approximately 0.25 mg/m<sup>2</sup>, the total adsorbate level at equilibrium is expected to be approximately 1.3 mass %.

The equilibrium adsorption results in Figure 4 help define the atmospheric moisture conditions required to limit adsorption by oxide after firing. The [H<sub>2</sub>O]<sub>s</sub> curve rises sharply at low humidity and then remains rather constant until the moisture level exceeds 50% RH. In order to significantly reduce the level of adsorption by controlling the atmospheric water concentration, the moisture level must not exceed 100 ppm (0.3% RH). If this condition cannot be rigorously maintained, the value of moisture-control efforts should be carefully examined because little is lost by having a relative humidity as high as 50%.

Adsorption Rates. Evaluation of kinetic data for adsorption of atmospheric water shows that the process occurs in distinct sequential steps. This result is important in defining procedures for obtaining representative samples for LOI analysis. Severe inhomogeneity would occur in the bulk oxide if the outer surface became saturated while portions of the material remained water-free. This occurrence is, however, precluded by the stepwise nature of water adsorption. During the first and second adsorption steps, the maximum concentration gradient within the sample is 0.1 mg H<sub>2</sub>O/m<sup>2</sup>, which corresponds to a maximum uncertainty of ±0.025 in the LOI result for oxide with an SSA = 5 m<sup>2</sup>/g. Blending of the oxide is advisable to minimize sampling problems, but LIO results for previously homogenized oxide should not be seriously in error.

Estimation of the time period that fired oxide can be exposed to a given atmosphere is important for establishing conditions and procedures required for packaging operations. Since the linear penetration rate of the initial adsorption reaction at different humidity levels is defined by Equation (3), the time to complete the initial adsorption step (0.1 mg H<sub>2</sub>O/m<sup>2</sup>) can be estimated if the oxide depth and humidity are known. For a



typical package (4 kg of PuO<sub>2</sub> at 2 g/cm<sup>3</sup> bulk density in a 11.5 cm diameter cylindrical container), the oxide depth is approximately 20 cm. The calculated times to complete the initial step (adsorb 0.05 mass % on a 5 m<sup>2</sup>/g oxide) for this configuration at 1, 10, and 50% RH are 20, 10, and 7.4 hr, respectively. Since these results are based on limited tests with small oxide samples, their validity should be verified with kilogram-size quantities of oxide prior to process implementation.

Significant advantage is gained by placing the oxide in a desirable configuration during cooling and handling. For example, if 4 kg of oxide is spread in a boat at an average depth of 5 cm, completion of the first adsorption step is expected in approximately 1.8 hr at 50% RH. Results of tests with covered PuO<sub>2</sub> suggest that a ten-fold reduction in the adsorption rate is achieved by covering the oxide to restrict communication with the handling atmosphere.

Knowledge of the stepwise adsorption process also allows simple laboratory procedures to be used in determining specific surface areas of plutonium dioxide. As described in this study and demonstrated by the results in Figure 3, measurement of the mass-time behavior of an oxide sample is easily achieved using a laboratory balance. First-order analysis of the rate-time data as shown in Figures 5 and 6 defines the time period required to complete the first adsorption step of 0.11 mg/m<sup>2</sup> and permits the corresponding mg/g loading for that step to be determined from the mass-time data. For example, the lnR-t data presented in Figure 5 for oxide fired at 950 °C shows that the initial step is complete after 0.5 hr. Corresponding data in Figure 3 show an adsorbate level of 0.57 mg/g at this point. Combination of these results yields a specific surface area of 5.2 m<sup>2</sup>/g, a value in good agreement with the 4.8 m<sup>2</sup>/g BET result. Similar procedures may be used to measure the SSA values of unfired oxide by drying at 100 °C and determining the time to adsorb one molecular layer of water, but appropriate humidity levels and measurement frequencies are necessary to ensure adequate loading and resolution.

LOI Analysis. Conditions are defined for using standard gravimetric methods to quantify residual adsorbate levels. Accurate analyses are obtained by firing 0.5 g oxide samples to constant mass at 950 °C in air. However, sensitivity is enhanced by using larger samples and complete desorption is ensured by firing at 1000 °C.

Precautions. Since experimental data from this study and from literature sources were obtained using high-purity dioxides, the results may not apply to all "oxides" that satisfy the storage requirement of 50 mass % Pu.<sup>8</sup> As suggested by the behavior of oxide prepared by calcining oxalate from chloride solution, important properties are expected to vary with process history and purity of the material as well as with the nature

of the impurities. Therefore, conditions and procedures described in this report should be validated for specific materials and equipment prior to their implementation in repackaging operations.

## CONCLUSIONS

Results of this study demonstrate that prior knowledge of plutonium oxide chemistry is inadequate for current needs and also suggest that certain information may be inaccurate. Such conclusions must seem incredible in light of the extensive investigations conducted on the plutonium-oxygen system over the past fifty years. However, a significant implication of this work and of on-going companion studies is that plutonium dioxide is thermodynamically unstable in air. Several independent observations suggest that  $\text{PuO}_2$  reacts with water over a substantial temperature range to form hydrogen and a higher-stoichiometry oxide containing Pu(IV) and Pu(VI). Conflicting observations made during the course of this study are reconciled if this reaction occurs.

The significance of forming a superstoichiometric oxide,  $\text{PuO}_{2+x}$ , by the reaction of dioxide with water may extend beyond pressurization of storage containers to include transport of plutonium in the environment. The existence of a facile route to hexavalent plutonium may be related to discrepancies between the thermodynamically predicted and observed oxidation states of Pu in aqueous media. Solutions in contact with  $\text{PuO}_2$  are reported to contain predominately Pu[VI] and lesser amounts of Pu[IV],<sup>24</sup> and the soluble plutonium species found in burial-ground seepage water from the dioxide is 75% Pu[VI].<sup>25</sup> Although subsequent studies of solutions equilibrated with  $\text{Pu}(\text{OH})_4$  indicate the presence of Pu[V],<sup>26</sup> uncertainties remain and the dissolution process may involve leaching of high-oxidation-state ions from the solid. Resolution of these issues rests in large measure on definition of the equilibrium plutonium-oxygen system<sup>27</sup> and on establishing the relative stability of plutonium dioxide and tetrahydroxide.

Additional issues remain to be addressed before the storage behavior of plutonium dioxide can be fully interpreted and predicted. Although radiolysis of water is apparently slower than the recombination rate of hydrogen and oxygen,<sup>18</sup> characterization of the chemistry and kinetics of reactions involving dioxide and water is essential for evaluating container pressurization during extended storage. The temperature and LOI dependencies of the hydrogen generation rate from chemical reaction are especially important. Several aspects of water adsorption, including the kinetic behavior of oxide obtained by calcining oxalate from aqueous chloride, are not understood. Alternatives to

LOI analysis should be developed with emphasis on proton nuclear magnetic resonance (NMR) and other methods that quantify hydrogen concentration.

However, conditions are adequately defined for preparing, handling, and certifying high-purity PuO<sub>2</sub> prior to storage. The excellent agreement observed between experimental results and literature reports confirms the results and conclusions of this study. Calcination of oxide at 950 °C effectively removes water and other adsorbates, reduces the specific surface area to a level that prevents excessive re-adsorption of water, and decreases the source term for environmental dispersal. Although several aspects of the adsorption and desorption behavior of the oxide remain undefined and certain conclusions drawn in the study need verification, essential information is presented for developing and implementing a packaging process that complies with the DOE standard for safe storage of plutonium dioxide.<sup>8</sup>

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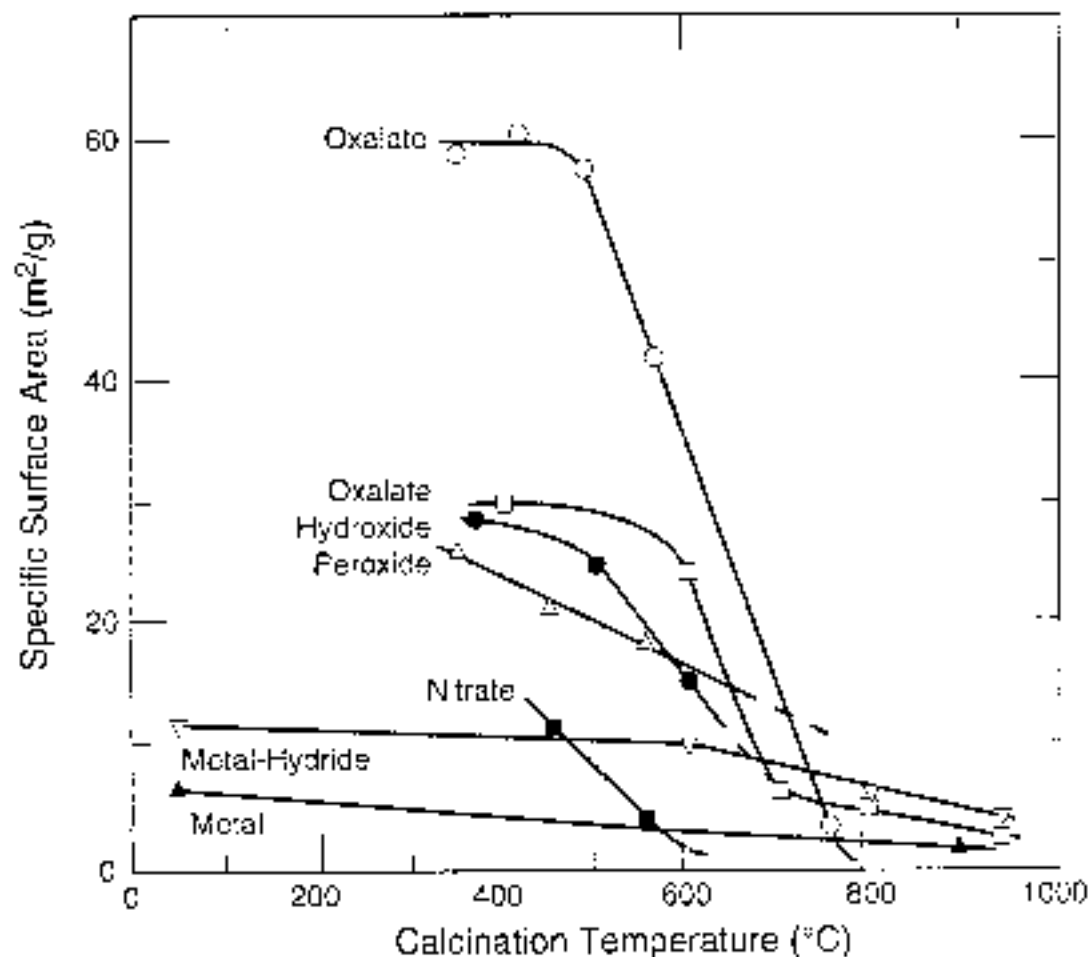


Figure 1. Dependence of the specific surface area of plutonium dioxide from different processing sources on calcination temperature. Data for oxide from metal are from Reference 5 and those for oxides from nitrate, peroxide, hydroxide and oxalate (open circles) are from Reference 11.

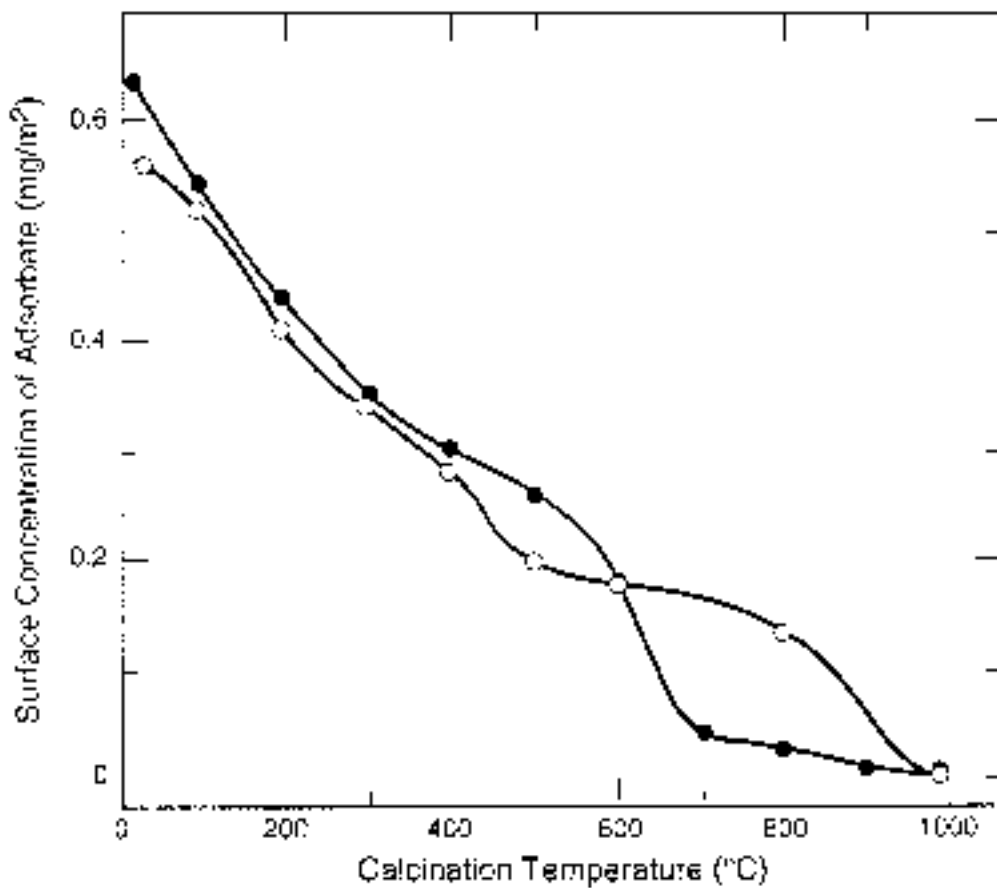


Figure 2. Temperature dependence of residual adsorbate concentration on plutonium dioxide. Data for oxide after extended exposure to air (solid circles) are from Reference 4 and those for oxide after exposure to water vapor (open circles) are from Reference 5.

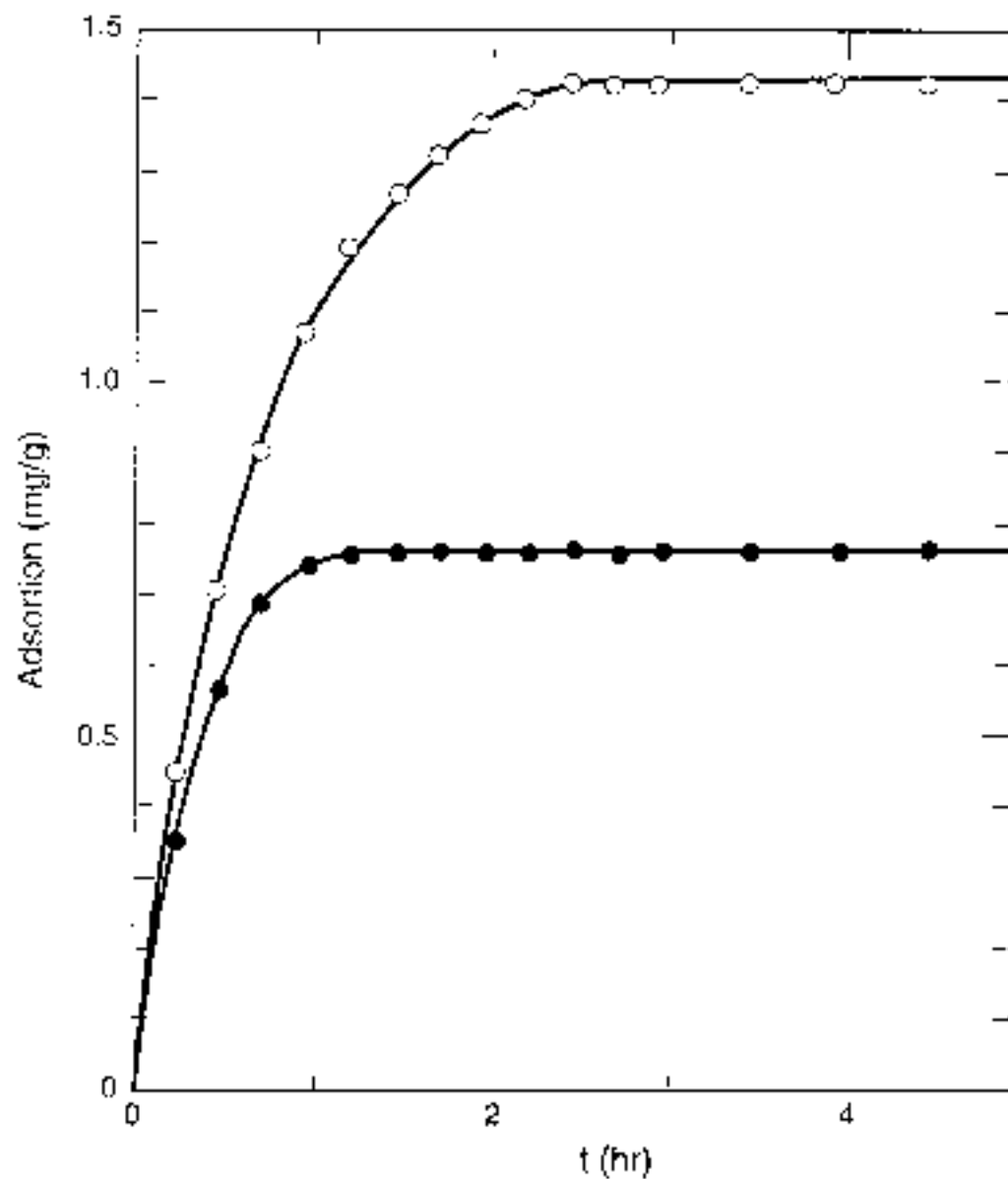


Figure 3. Time dependence of the adsorbate mass on plutonium dioxide exposed to air at room temperature and 1% relative humidity. Data for oxide from metal calcined at 700 and 950 °C are indicated by open and solid circles, respectively.



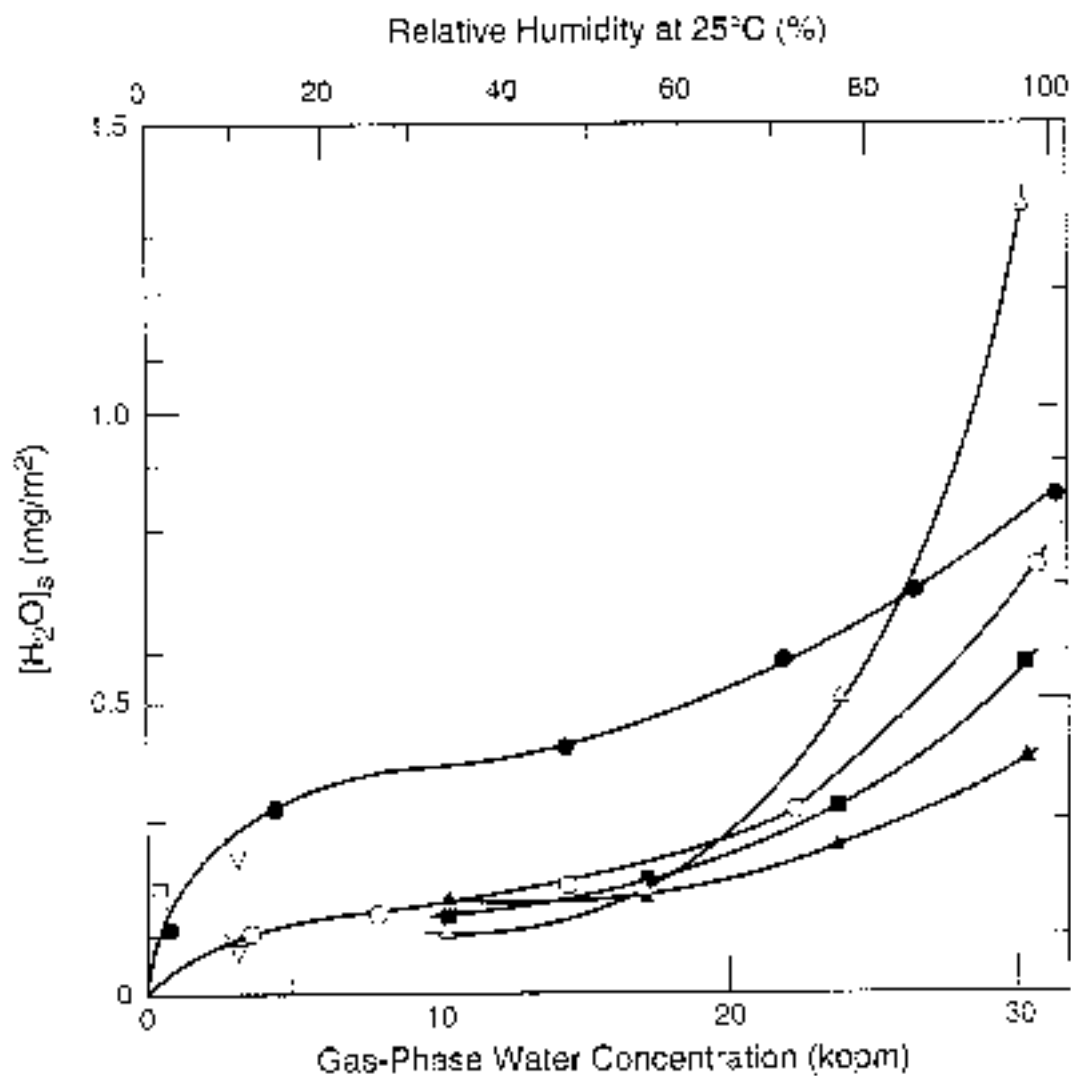


Figure 4. Humidity dependence of the equilibrium water concentration on plutonium dioxide dried or heated at 100 °C (lower set of curves) and fired at 900 to 950 °C (upper curve). Data indicated by open and solid circles are from References 5 and 12, respectively; those indicated by solid squares and by upright triangles are from Reference 11.

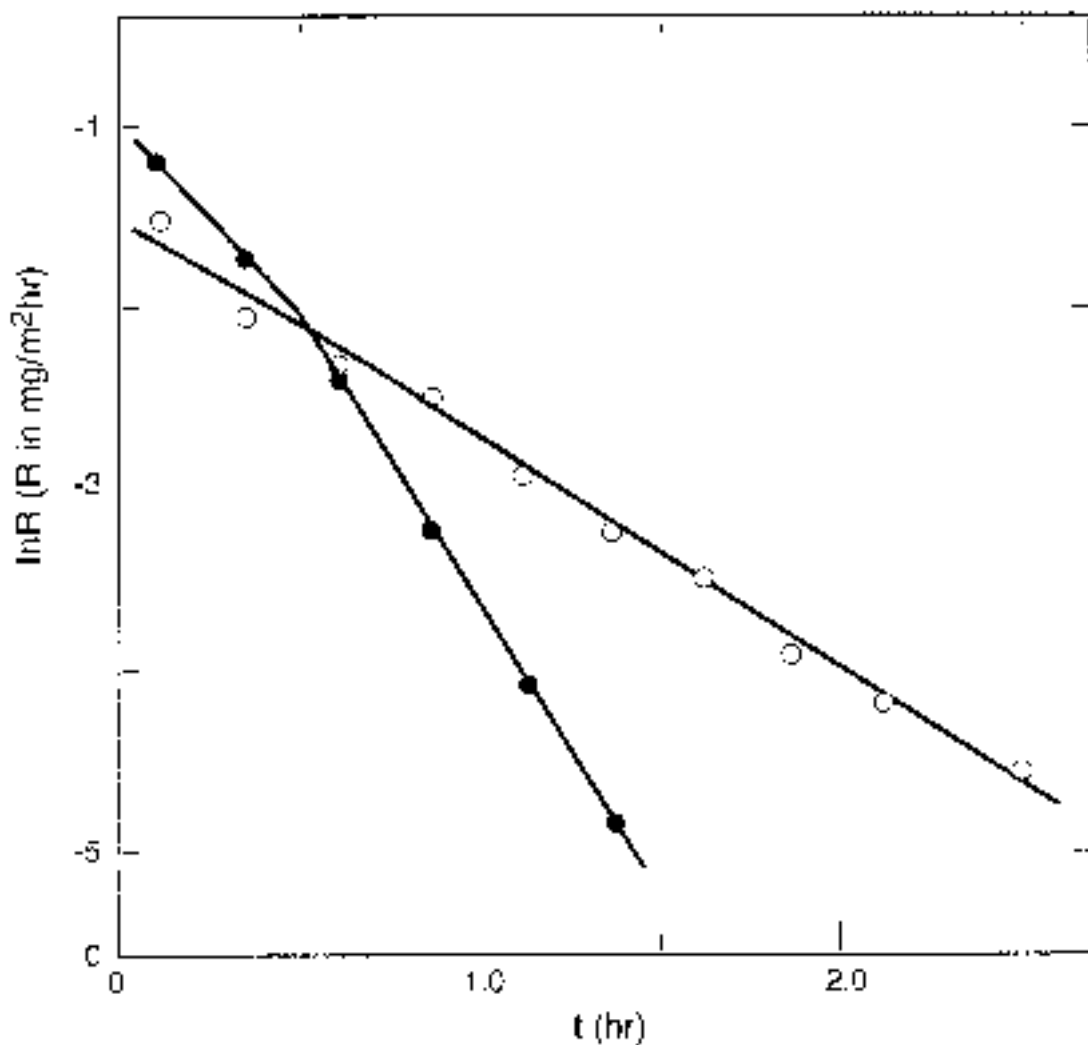


Figure 5. First-order analysis of adsorption rate data for plutonium dioxide from metal exposed to air at room temperature and 1% relative humidity. Data indicated by open and solid circles are for oxide fired at 700 and 950 °C, respectively.

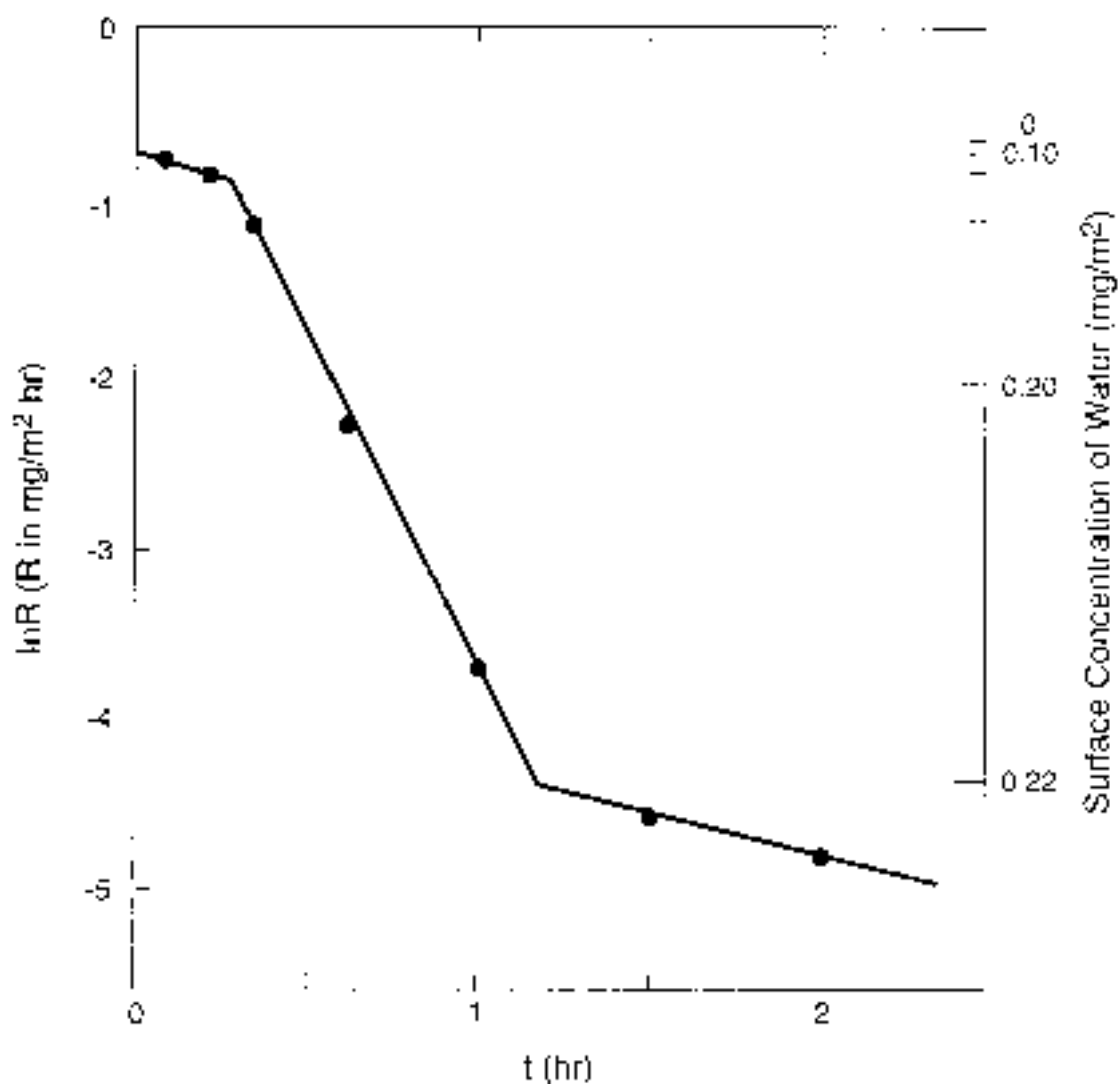


Figure 6. First order analysis of adsorption rate data for plutonium dioxide from oxalate exposed to air at room temperature and 10% relative humidity. The oxide was fired at 700 °C prior to exposure.

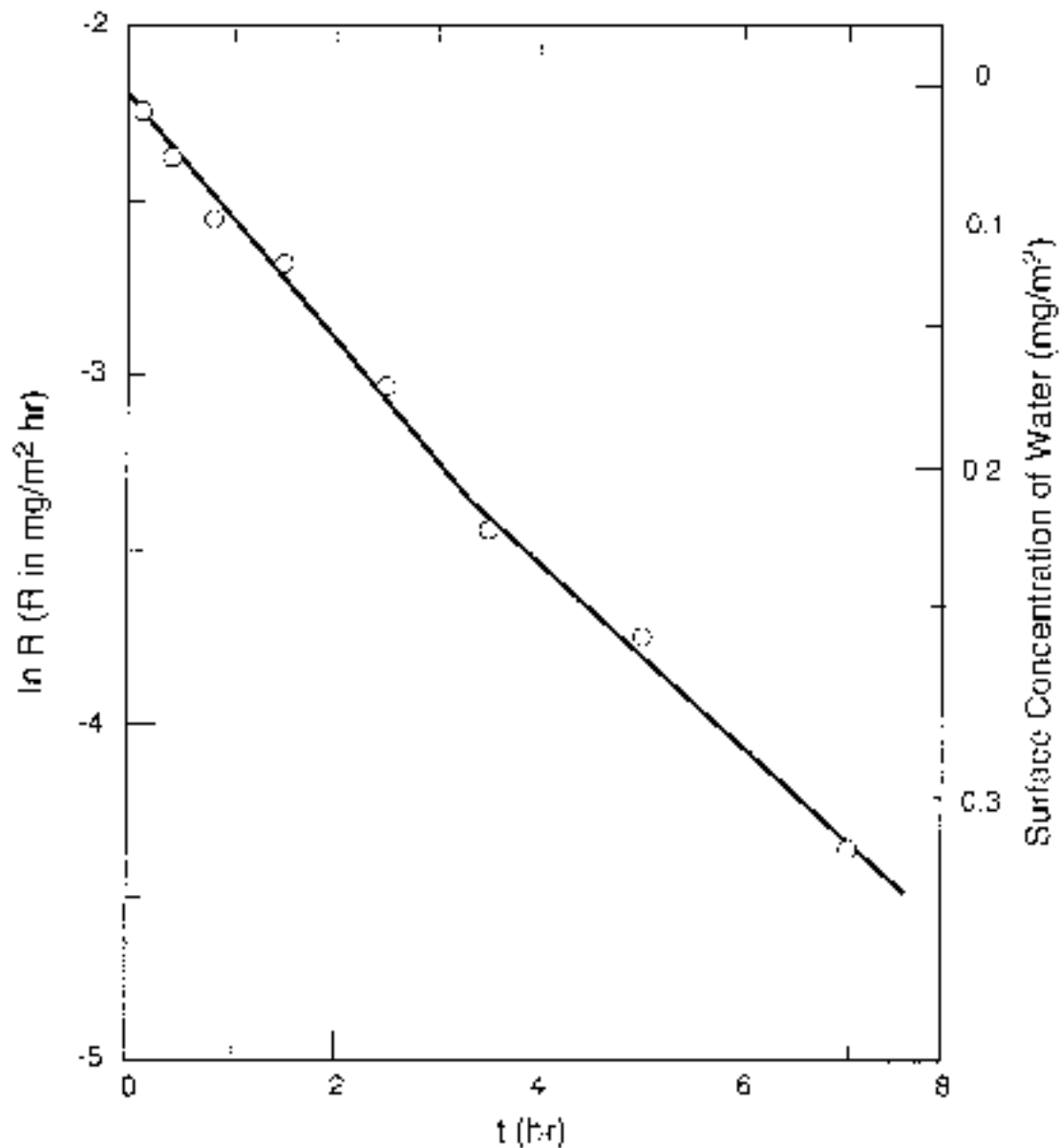


Figure 7. First-order analysis of adsorption rate data for dried plutonium dioxide exposed to air at room temperature and 76% relative humidity. The data are derived from graphical results presented in Reference 11.

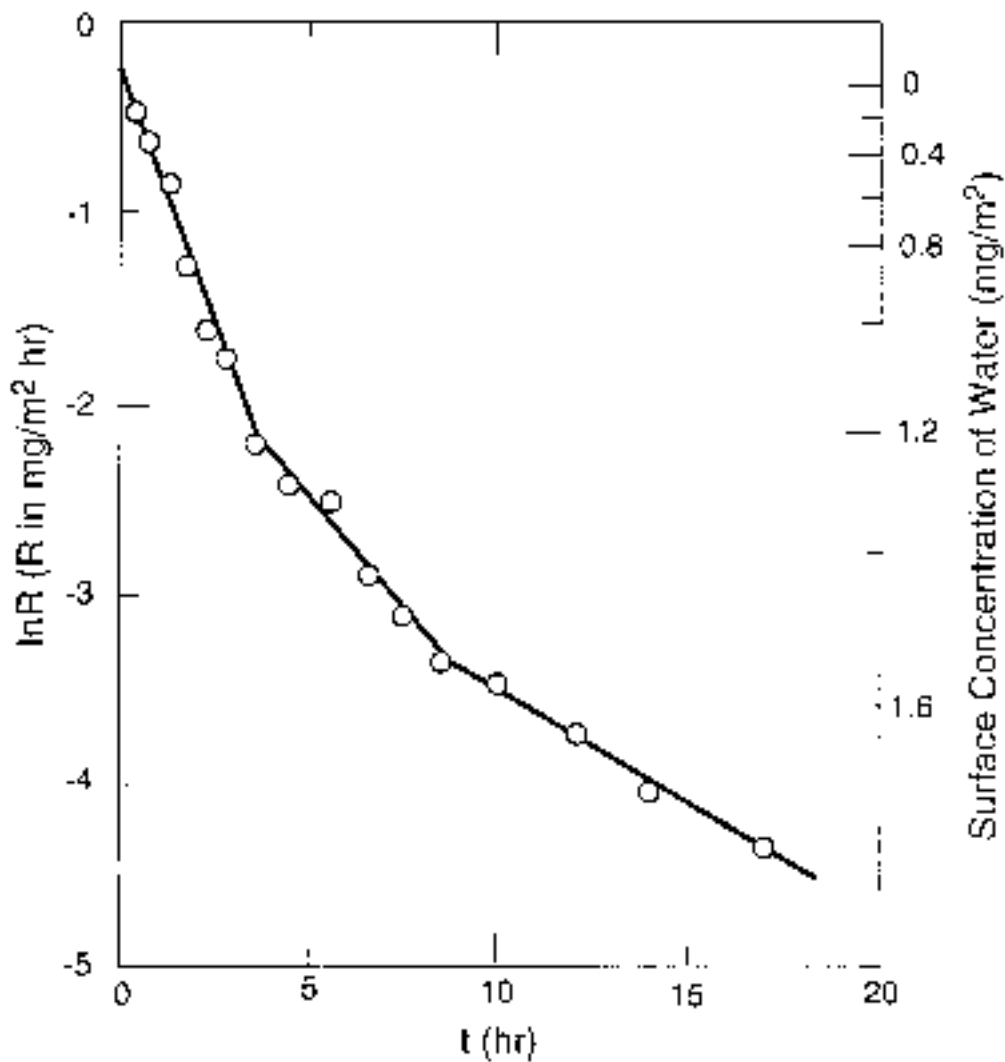


Figure 8. First-order analysis of adsorption rate data for plutonium dioxide exposed to air at room temperature and  $98 \pm 2\%$  relative humidity. The oxide was dried in a stream of 5% relative humidity air prior to exposure. The data are derived from graphical results presented in Reference 3.

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