

THE SCIENTIFIC BASIS FOR PLUTONIUM STABILIZATION WITH PARTICULAR EMPHASIS ON GAS GENERATION

Luis Morales¹, Robert G. Behrens¹, John Lyman², Lav Tandon¹, Jack Kennison¹ and Mark Paffett²

¹ Nuclear Materials Technology Division,

² Chemical Science and Technology Division,

Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

The Department of Energy/Environmental Management (DOE/EM) is the nations steward for management of a vast array of nuclear materials which are considered excess to national security needs as well as excess to other DOE programs. This stewardship role involves management of the entire excess inventory of fissile materials at RFETS, Hanford, Savannah River, and other DOE sites. Accordingly, DOE/EM must ensure that the domestic management, use storage, and disposition of nuclear materials under its stewardship are conducted in an efficient, secure, and environmentally safe manner. Furthermore, DOE/EM must be an active participant, with other DOE Programs Offices, as an enabler and patron of nuclear materials science in order to sustain a national resource of scientists who are knowledgeable in the physi-chemical properties of DOE/EMs nuclear materials inventory. Maintaining a strong scientific base and capability will allow DOE/EM to resolve long term storage, transportation, and disposition issues with the nuclear materials under its stewardship as issues and problems arise.

In this manuscript we address specific physico-chemical processes and transformations that have relevance to gas generation and storage of actinide materials. These chemical and physical processes and experiments are designed to measure unknown or ill-determined thermochemical and radiolytic parameters. These parameters are utilized in developing mathematical models of gas generation of relevance to storage of actinide bearing materials. The ultimate goal of this endeavor is to predict safe storage conditions based upon initial bounding conditions, processing steps, and known test case scenarios. The essential elements of this work are encompassed in three sections: 1) thermochemical properties and parameters of adsorbed water on actinide oxide surfaces relevant to chemically evolved gases; 2) known radiolytic pathways and rates for production of gases from bulk water, gas phase water and adsorbed water; and 3) modeling efforts that encompass all of the these events (where known or measured) occurring in storage scenarios to predict gas generation in actual repository scenarios. Through incorporation of all the pertinent events likely to occur in well-defined actinide storage scenarios, safe bounding conditions of gas stoichiometry and pressure are expected to predominate (although not all processes and rates are completely understood). Suggested further work and current experimental efforts to complete this picture are also identified.

Introduction and Scope of Problem

The Department of Energy/Environmental Management (DOE/EM) is responsible for the management and long-term disposition of a variety of materials located at RFETS, Hanford, Savannah River, and other DOE sites. The new plutonium storage standard, set to replace DOE 3013 requires thermal stabilization of the materials prior to packaging for storage. The Pu content of those materials can vary from ~86 weight percent, (essentially pure PuO₂), down to ~30 weight percent. With such a range of composition, the presumed plutonium dioxide can be in contact with a variety of other materials. Typically, these "impurities" include alkali metal chlorides, MgCl₂, CaCl₂, MgO, Fe₂O₃ and other materials that are not well characterized. In addition, these solid mixtures are in contact with the gas phase under which the materials were packaged and the moisture content may not be known or well controlled. The new plutonium stabilization standard does not set accepted glove-box moisture levels nor does it prescribe the time duration between calcination and packaging.

The DOE's standard method, DOE-STD-3013-96 and its proposed revision, for stabilizing pure and impure actinide materials is by calcination in air followed by sealing the material in welded stainless steel containers [1]. The 3013 standard contains an equation that predicts the total pressure build-up in the can over the anticipated storage time of fifty years. This equation was meant to model a worst-case scenario to insure pressures would not exceed the strength of the container at the end of 50 years. As a result, concerns about pressure generation in the storage cans, both absolute values and rates, have been raised with regard to rupture and dispersal of nuclear materials [2]. Similar issues have been raised about the transportation of these materials around the complex.

Adequate scientific resources must be available to DOE/EM in order to understand the physical and chemical environment under which excess nuclear materials are packaged, stored, transported and dis-positioned. In order to approach such a daunting task, experiments on carefully selected, representative chemical systems and a cooperative modeling effort are required. This combined approach must incorporate core scientific resources in the following areas: thermodynamics, kinetics, radiation chemistry, surface science, materials science, solid-state chemistry, and solid-gas chemistry in order to identify, study and perhaps prevent and/or mitigate the pertinent chemical reactions which may lead to problems during long-term storage or transport of fissile materials.

Thermochemistry of absorbed water on actinide oxide surfaces

In the areas of plutonium waste disposition and storage, and medium to long term retrievable Pu materials storage, the issue of water and other small molecule interactions with pure or impure Pu oxide materials and metal has become a major concern. Small molecule reactions in these types of systems have led to changes in materials stoichiometry, containment breaches and dispersal of material resulting from pressurization, corrosion of the containment, and the collapse of sealed containers due to the formation of partial vacuum. The exact nature of these reactions and the resulting implications for medium to long term storage are not well understood, although there

have been studies which attempted to explain them from a large body of observations and experiments [3-6].

Residual water adsorbed on and in actinide oxide materials following calcination is known to ultimately lead to gas generation through a variety of physical and chemical mechanisms. We begin by describing results and molecular details involved in both reversible and irreversible adsorption/desorption of water at actinide and actinide oxide surfaces. Both the molecular level understanding and the thermodynamic properties of these transformations will ultimately find their way back to encompassing modeling efforts that are intended to predict the time dependent properties of gas buildup and limiting (equilibrium) values of gas pressure and stoichiometry.

The starting point for water adsorption is the reversible adsorption of multi-layer water on oxide surfaces. A schematic of this process and other related processes described below is shown in Fig. 1.

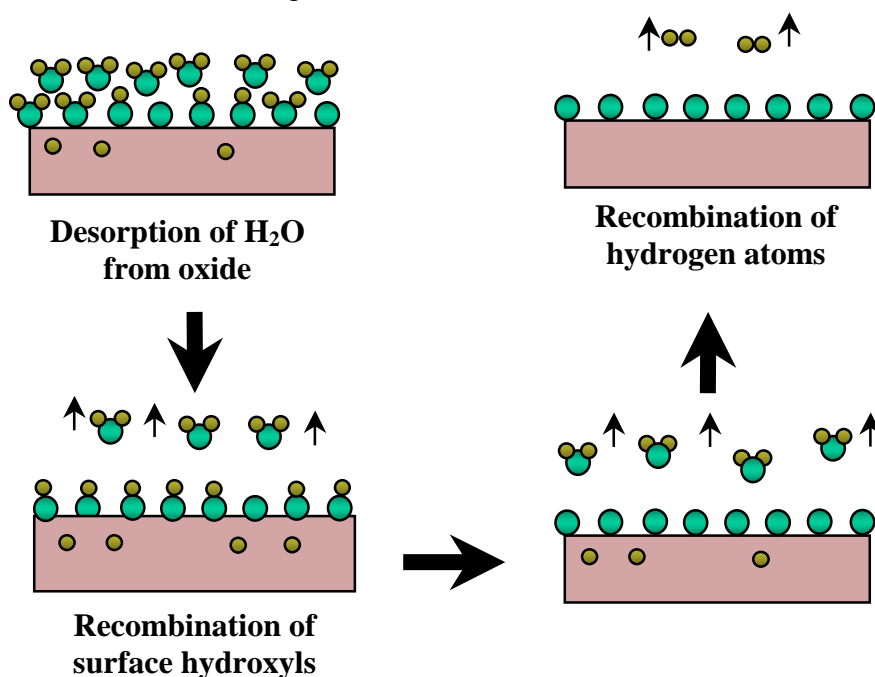
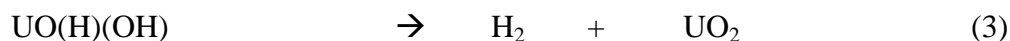
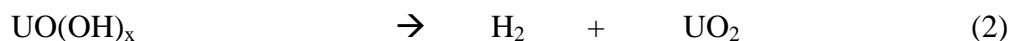
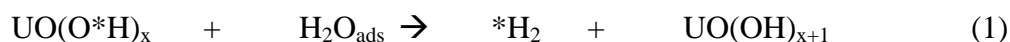


Fig. 1. Physical and chemical processes generating gaseous species following water adsorption on actinide and actinide oxide surfaces.

A large number of oxide surfaces have been examined for water adsorption [7 and references contained therein]. In most cases the desorption enthalpy (equivalent to the adsorption enthalpy for a non-activated process) is known to be on the order of 41.8 to 50 kJ M⁻¹. Bear in mind this is for water that does not originate from any additional bond forming steps. For specific surfaces that are noted to develop extended hydrogen bonded networks (e.g. surfaces with high concentration of surface hydroxyls) desorption enthalpies for water have been noted in certain circumstances to increase to ~80 kJ M⁻¹. Several reports have examined the interactions of water with Pu oxide and U oxide surfaces [3,4,8,9]. In early work by Stakebake [8], the desorption enthalpy of water from PuO₂ (presumably the hydroxylated surface) was determined to be ~ 84.0 kJ M⁻¹. Other

water desorption (generation) processes were suggested in this work and have been recently reinvestigated [10,11]. Re-examination of water interactions at PuO₂ surfaces clearly indicate the importance of surface hydroxyl species and possible surface hydroxyl recombination events that lead to both H₂ and H₂O generation mechanisms (Fig. 1). In fact, a correct re-determination of the higher temperature (desorption ~ 380 K) water desorption state observed in Stakebake's work, arising from recombination of surface hydroxyls, indicates that an activation energy of ~170 kJ M⁻¹ is more appropriate than the initial estimate of 284 kJ M⁻¹.

Recent publications and related work on water interactions with uranium and uranium oxide surfaces have also revealed a number of molecular details that have immediate parallels with the corresponding Pu systems [9]. These studies of the interactions of D₂O with uranium metal (and oxide) at various surface temperatures have been performed using surface specific techniques of thermal desorption mass spectroscopy (TDMS), ultraviolet photoelectron spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS), and static secondary ion mass spectroscopy (SSIMS). The kinetics of water desorption have been directly measured to be ~45 kJ M⁻¹ for water desorption from planar monolithic UO₂, 45-48 kJ M⁻¹ from hydroxylated UO₂, and hydrogen generation mechanisms arising from surface reaction with adsorbed water, recombination of hydroxyl groups, and recombination of adsorbed hydrogen and surface hydroxyls have been observed. These hydrogen generation steps are denoted in equations 1 - 3 and have an existing parallel in the suggested water corrosion mechanism of PuO₂ in the presence of O₂ (discussed below and in the modeling section).

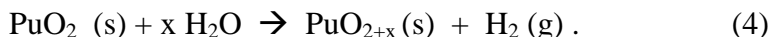


The net conclusion of these studies is that frequently a mixed metal oxide and hydroxyl surface is created following water interactions and through a combination of chemical and radiolytic reactions, H₂ gas can also be generated. In most initial bounding conditions for actinide oxide storage vessels the partial pressure of water and temperature clearly indicate that adsorbed multi-layers of water will be present. The kinetics of water desorption from clean oxide, surface hydroxide and from water multi-layers are all readily measured parameters that provide initial values for gas generation modeling of actinide oxide storage vessels. A number of chemical and physical gas generating processes have been delineated and although some suggested mechanistic steps are potentially debatable, the major gas creation processes are fairly well known and provide input for the modeling endeavor described below.

The interaction of PuO₂ powders with water has been investigated from 373 K to 623 K using a suite of experimental techniques which include: microbalance and pressure-volume-temperature (PVT) methods, thermal gravimetric analysis (TGA), mass spectrometry (MS), x-ray and neutron diffraction. Reaction rates and oxide compositions were determined from measured increases in sample mass or pressure over time (t).

Gaseous and solid products were analyzed using MS and diffraction methods, respectively. Oxide products have also been characterized by x-ray photoelectron spectroscopy (XPS). The plutonium oxide specimens used in this study were formed by oxidation of electro-refined alpha-phase metal containing approximately 100 ppm Am as the major metallic impurity. The specific surface area of the oxide was 4.8 m²/g. The initial oxide stoichiometry was determined to be PuO_{1.97} based on the measured lattice parameter and data from the correlation of the cubic lattice parameter (a₀) at fixed O:Pu ratios with temperature reported by Gardner et al. [12].

PVT and microbalance measurements were made at 473 K to 623 K using techniques similar to those described for kinetic measurements at 298 K [13]. Results of PVT and microbalance measurements during exposure of plutonium dioxide to water vapor at 473 K to 623 K and 24 Torr show linear increases in pressure and mass as a function of time. This behavior indicates that water is irreversibly reacting with the Pu oxide. Mass spectrometric analysis of gas samples taken after termination of the tests show that only H₂O and H₂ were present in the gas phase. These results are identical to those observed at 298 K [13] and suggest the following reaction:



This equation implies that a fraction of the plutonium is oxidized to an oxidation state greater than Pu(IV); although difficult to unambiguously prove in an ex-situ setting, this result is consistent with earlier XPS data [4]. An Arrhenius analysis of the rate data derived from the slopes of the P-t curves and the specific surface area of the oxide is shown in Figure 2. The rate at 298 K is a value obtained from three independent kinetic measurements for the PuO₂ + H₂O reaction [13]. The kinetic results from the microbalance and PVT measurements are described by a single relationship:

$$\ln R = -6.441 - (4706/T) . \quad (5)$$

The activation energy (E_{act}) for reaction 6 is 39.3 +/- 2.5 kJ M⁻¹. The uncertainty in E_{act}, results primarily from the uncertainty in the average R at 298 K [13]. Rates from microbalance measurements are in good agreement with those from PVT data, but are consistently higher because of water adsorption on the microbalance and the sample.

X-ray and neutron diffraction data show that the oxide product formed during reaction (4) has a fluorite-related fcc structure derived from that of the dioxide. The

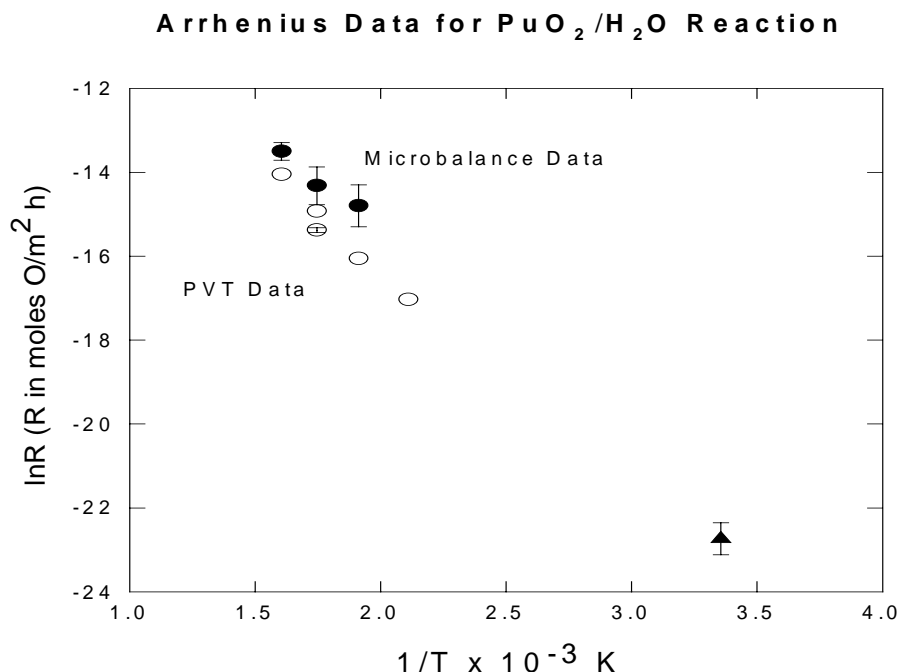


Figure 2. Arrhenius results for the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction from 298 to 623 K. Microbalance and PVT data are shown by filled circles and open circles, respectively. The 298 K data point, represented by a filled triangle, is from a prior PVT study [13].

The results of eight measurements with calculated O:Pu ratios from 2.016 to 2.169, show that the lattice parameter of PuO_{2+x} is a linear function of composition:

$$a_0 (\text{\AA}) = 5.3643 + 0.01764 \text{ O:Pu.} \quad (6)$$

When the PuO_{2+x} oxide product was heated above 673 K in subsequent TGA experiments, a mass loss was observed at approximately 633 K and the lattice constant of the resulting oxide returns to that of PuO_2 , indicating that PuO_{2+x} is stable only up to 633 K. The O:Pu ratio calculated from the measured mass loss in the TGA experiments and the hydrogen generation from the PVT experiments are in excellent agreement.

Kinetic results for oxidation of plutonium dioxide by water show that the reaction has a prominent temperature dependence from 298 K to 623 K. The temperature dependence observed for the rate demonstrates that the reaction of PuO_2 with H_2O is primarily chemical instead of radiolytic. The rate of a purely radiolytic process is expected to be temperature independent at a fixed water pressure. At isobaric conditions, the measured activation energy of a radiolytic process might actually be slightly positive because the rate is expected to decrease as the equilibrium surface concentration of H_2O adsorbed on the oxide decreases with increasing temperature. If formation of PuO_{2+x} is promoted by radiolysis of H_2O , the largest fractional contribution to the oxidation rate is anticipated at low temperature in a system with a high surface concentration of water.

Vegard's law behavior (Equation 6) assists in defining important solid-state properties of PuO_{2+x} . The continuous variation of a_0 with stoichiometry indicates that O

in the PuO_{2+x} structure exists as a solid-solution. Neutron diffraction studies indicate that additional oxygen is accommodated on interstitial sites in the fluorite lattice of PuO_2 . Whereas oxidation of Pu(IV) on cationic sites of dioxide would tend to shrink the lattice, accommodation of oxide ions on vacant sites causes lattice expansion. The opposing changes are apparently of comparable magnitude and the net effect is a low dependence of a_0 on the composition of PuO_{2+x} .

Comparison of results for Pu-O and U-O systems suggests that the hyperstoichiometric regions above the dioxide compositions differ substantially. Although early work on the uranium system indicated the existence of a cubic UO_{2+x} solid solution at O:U ratios up to 2.33, subsequent studies show that UO_2 coexists in equilibrium with the tetragonal U_4O_9 phase at temperatures below 573 K, and that the UO_{2+x} phase is stable only at elevated temperatures [5]. Cubic lattice parameters measured for the metastable UO_{2+x} product suggest that a_0 decreases with increasing composition. Although UO_{2+x} and PuO_{2+x} apparently have similar structures, it is evident that the uranium oxides are not a suitable model for phase equilibria of PuO_{2+x} .

In addition to the physical adsorption and (ir)reversible chemical steps described above that generate gas, other gas phase reactions can occur that are catalyzed by actinide (and others elemental) oxide surfaces. Specifically, the reaction of $\text{H}_2 + \text{O}_2$ has also been explored over actinide oxide surfaces and adds an additional mechanistic step that serves to both lower overall gas pressure and reduce the hazardous gas potential in actinide oxide vessels.

Rates of Kinetic Processes Relevant to Chemically Evolved and Radiolytically Generated Gases

The technical basis for the pressure equation given in the 3013 standard mentioned in the introduction has not been fully established. The pressure equation contains two major assumptions, (a) that hydrogen and oxygen generated from radiolysis do not react to form water and (b) that the oxygen initially present following packaging reacts with the oxide material and does not contribute to the pressure in the container. With regard to the first assumption, if the formation of water from hydrogen and oxygen is important, then the calculated pressures would be dramatically reduced. The formation of water is thermodynamically favored and can be assisted catalytically by the presence of a variety of materials in the containers. In addition, the corporate knowledge from shelf-life programs around the complex is that most containers do not show signs of extreme pressurization.

The recombination rates of hydrogen/oxygen mixtures in contact with pure and impure plutonium oxides were measured in order to provide a stronger technical basis for the 3013 standard. The goal of these experiments was to determine whether the rate of recombination is faster than the rate of water radiolysis under controlled conditions. This was accomplished using a calibrated pressure-volume-temperature (PVT) apparatus to measure the recombination rates, in a fixed volume, as the gas mixture was brought into contact with oxide powders at temperatures between 323 and 573 K. In addition, a 2 % H_2 /air mixture encompasses typical scenarios in which the cans are sealed in air and form various amounts of hydrogen over time. These conditions were selected in order to bracket the temperature conditions expected in a typical storage can. Pressure-time curves

and mass spectrometric results were obtained during gas mixture exposure to pure and impure plutonium oxides. The pure oxide was obtained from oxidation of alpha phase plutonium metal. The impure oxide was obtained through the Defense Nuclear Facilities Safety Board (DNFSB) 94-1 R & D program's Materials Identification and Surveillance (MIS) project and selected due to its low plutonium content (29 w/o) and its high chloride content (18 w/o). Analysis by x-ray powder diffraction shows that the impure oxide examined is a mixture of plutonium dioxide, sodium chloride and potassium chloride.

Figure 3 compares the kinetic data for the pure oxide, on a time scale of 0 to 600 minutes, with the kinetic data for the impure oxide collected at 473 to 573 K. These data show that the rates of water

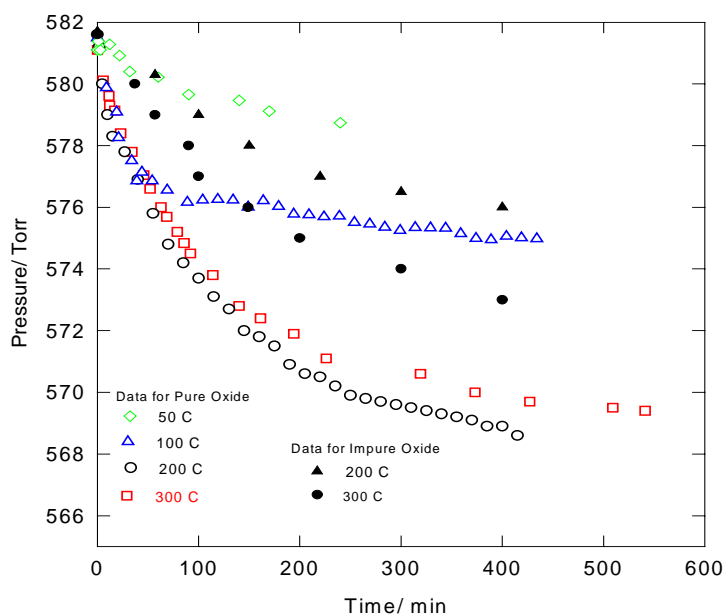


Figure 3. Plots of the measured pressure-time curves for both the pure and impure Pu oxides. A finer time scale is employed to show the details of the data collected early in the experiments.

formation at the higher temperatures for the pure oxide are essentially the same, 4.59×10^{-4} mol $\text{H}_2\text{O}/\text{m}^2$ day, based on the initial slopes of the pressure-time curves. Only the data collected at 323 K for the pure oxide show deviation from this behavior with a rate of 6.63×10^{-5} mol $\text{H}_2\text{O}/\text{m}^2$ day. The recombination rates for the impure oxide at 473 and 573 K were 1.30×10^{-4} and 2.63×10^{-4} mol $\text{H}_2\text{O}/\text{m}^2$ day, respectively. The data for the 373 K run for the pure oxide clearly show a sharp break in the slope approximately 100 minutes into the experiment. In addition, the data collected at 573 K for the pure oxide show an upturn after approximately 1000 minutes into the experiment. This upturn then levels off and remains constant for ~20 days, until the experiment was terminated.

The experiments suggest that the oxide surface is an active catalyst for the recombination reaction. The concentration of active surface sites governs the kinetics of

recombination early on, and as the reaction proceeds, certain moieties (OH or H₂O for example) are suggested to occupy these surface sites thereby reducing the rate of recombination. Above 573 K enough thermal energy is provided to maintain a larger fraction of the active sites available for recombination. The prominent break in the 573 K pressure-time curve shows how dramatically the recombination rate is reduced when the active sites become blocked. This type of behavior would not be expected for a recombination reaction dominated by radiolytic formation of radicals in the gas phase.

The results of these kinetic experiments demonstrate that steady-state gas compositions are reached indicating the rates of recombination and water radiolysis equalize under these experimental conditions, although the initial recombination rate is dramatically faster than the radiolysis of adsorbed water. For this particular gas mixture (2% H₂/air), the steady-state gas composition is calculated to be below the flammable limit.

The implication of this work on the extended storage of materials is that the recombination reaction is a chemical one involving heterogeneous surface catalysis and is not strongly driven by the radiolytic formation of radicals in the gas phase under these experimental conditions. Radiolytic processes may be involved to a certain extent in that alpha radiation may initiate or enhance surface reactions. Hydrogen plus oxygen recombination rates limit the potential pressure in the container caused by water radiolysis. The establishment of a steady-state gas composition in the 573 K and 323 K experiments on the pure oxide indicates that the rates of water radiolysis and recombination equalize.

The implication of these studies (the oxide/water reaction and H₂-O₂ recombination) to the storage issue is that the interplay between these processes is more clearly understood. Water, adsorbed on the PuO₂ surface, reacts to form hydrogen gas through a variety of mechanisms identified in this studies. If the gas phase contains oxygen, the recombination reaction will form water. The reaction of water and PuO₂ will continue until the equilibrium composition of PuO_{2+x} at a given temperature and hydrogen pressure is reached. If there is no oxygen in the gas phase to react with the hydrogen, then the gas phase is enriched with hydrogen. Again, this process will continue until the equilibrium composition of PuO_{2+x} at a given temperature and hydrogen pressure is reached or until the water, if it is the limiting reagent, is consumed. The important fact relevant to the storage issue is that a steady-state is reached. Therefore, the pressure reaches a steady-state value, which may be calculated from the properties of the materials involved and the pertinent chemical reactions. In order to carry out such calculations, both aspects, kinetics and thermodynamics, are required to properly address the long-term storage issues.

Radiolysis of Water

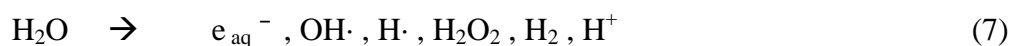
Gas generation arising from radiolysis is described by three distinct regimes within the containment vessel. These distinct areas include radiolysis of bulk water (multi-layer adsorbed water), radiolysis of gas phase water, and radiolytic driven processes occurring in the surface interfacial region with adsorbed water. We begin by describing the pertinent features of gas generation arising from bulk water. The deposition of energy by ionizing radiation in bulk water predominately leads to the

production of a free electron and the molecular cation (H_2O^+). Within a few picoseconds, the cation undergoes proton transfer with a neighboring water molecule to give an OH radical ($\text{OH}\cdot$) and a hydrated proton. These two products do not normally affect the production of molecular hydrogen and are generally ignored over limited time intervals. The free electron eventually comes to thermal equilibrium and hydrates to become the main reducing species in the radiolysis of water. Reactions of the hydrated electron (e_{aq}^- + e_{aq}^-) are considered the main source for the production of H_2 . Hydrogen atom + hydrogen atom reactions will also give molecular hydrogen, but hydrogen atom yields are usually less than 10% of e_{aq}^- yields and can be also ignored. This assumption is not valid in acidic conditions (and possibly at oxide surfaces) as e_{aq}^- entities are quickly converted to hydrogen atoms [14].

Recent experiments at University of Notre Dame with gamma (γ)-radiolysis have discovered that the pre-hydrated electron plays a very important role in the production of molecular hydrogen [15]. Calculations in progress suggest that most of the molecular hydrogen observed in γ -radiolysis is due to pre-hydrated electrons. The chemistry of pre-hydrated electrons is still relatively unknown because of their short lives and is an emerging area of research.

General Aspects of Water Radiolysis in Waste Packages

The new 3013 standard limits the thermal output in the waste packages to 19 watts (W). Other critical requirements are that organic materials be eliminated from the stored materials and that the moisture content be reduced to 0.5 wt% by calcination at 1223 K. For the representative MIS program samples the maximum observed thermal output was 10 W. For weapons grade PuO_2 , 10 W translates to a total dose of $\sim 10^9$ Gy over fifty-year lifetime. For a number of technical reasons, actual doses to the adsorbed water/moisture will always be dramatically lower than the maximum theoretical dose. Significant radiation damage in liquid water will lead to the formation of following radical, ionic, or molecular species (as major products):



Competition kinetics is applied to predict which of the competing reactions will predominate. Radicals are generally long lived with higher probability of reaction with the walls of the container and with other products. If there is dissolved oxygen present, species such as O_2^- and $\text{HO}_2\cdot$ also can be produced.

Because the decomposition mechanism of water does not directly depend on the nature of radiation, the yield of each radiolysis product is directly influenced by linear energy transfer (LET), which is much greater for alpha (α)-particles than for gamma (γ)-rays. A comparison of the G-values for the radiolysis of liquid water indicates that γ -radiation produces greater concentrations of e_{aq}^- , $\text{OH}\cdot$, and $\text{H}\cdot$, whereas α yields are higher for molecular species such as $\text{HO}_2\cdot$, H_2O_2 , H_2 , and H_2O [16-18]. For α -radiolysis of liquid phase water G (H_2) ranges from 0 - 1.6 molecules/100 eV [14,17,19-22]. The role of scavenger impurities such as NO_3^- , Cl^- , Br^- , and SO_4^{2-} with respect to the yield of G (H_2) is more pronounced for γ -irradiation than for α -irradiation [16,20,23]. Therefore, briefly summarizing this well studied field, the key variables that effect the

yield of various species listed above are electron scavenger concentration, time regime, temperature, pH, dose, dose rate, and LET. Alpha particle radiolysis of bulk water in Pu storage containers will produce a low steady state concentration of the molecular species H_2 and H_2O_2 [15,24,25].

The influence of actinide oxide particle size is anticipated to also have an important role in evolved gas generation. The range of an α -particle in PuO_2 is 12.9 μm and therefore only those alphas emitted from the outermost portion of most plutonium particles exit with energy approaching the full 5-6 MeV energy of the nascent α -particles as shown using our modeling codes and TRUPACT-II safety analysis reports [22,26]. The particle size distribution and mean diameter of the PuO_2 mass in water-containing materials after calcination at 1223 K is observed to exceed the range of α particles of weapons-grade materials [27,28]. The measurements on calcined representative materials from Hanford Plutonium Finishing Plant (PFP) and Rocky Flats Environmental Technology Site (RFETS) studied in the Materials Identification and Surveillance (MIS) program confirm this expectation. The energy of all other α emissions will be degraded by self-absorption. The consequence for adjacent adsorbed phases is that the delivered dose will be reduced severely below the maximum theoretical value. In addition, the energies of the α particles exiting PuO_2 particles is distributed over a continuum of energies, ranging down to nearly zero. The range of water using the TRIM program suggests a range for 5.15 MeV α -particles in water to be 38.6 μm which is in good agreement with the experimentally determined literature value of 38.9 μm calculated for 5.3 MeV α -particles emitted by ^{210}Po [17].

Gaseous water (and other) molecules situated in headspace and void regions of storage containers are expected to contribute to gas generation through gas phase radiolysis processes. The overall features of radiation-induced decomposition of water vapor are similar to the photochemical decomposition [17]. There is a large variation in molecular hydrogen yields reported for gaseous water due to dose, impurity, pressure, temperature, wall effects etc. A survey of the literature reveals for $G(H_2)$ from α -particle induced radiolysis of water vapor range from 0.06 – 5.9 molecules/100 eV [29]. These yields are expected to be relatively independent of LET because the low density of water vapor allows active species to diffuse from particle track before they can react together [17]. The radicals formed are longer lived with higher probability of reaction with the wall and other products and are therefore, converted to stable H_2 , O_2 , H_2O_2 and H_2O . According to the literature there should only be a low steady state concentration of molecular products such as H_2 and O_2 for both liquid and gases under constant irradiation in pure water vapor since back reactions play a key role. Some studies have suggested the formation of anions such as OH^- , O^- , H^- , and H_2O^- for adsorbed water [30]. These species are not normally observed for liquid water and can effect the H_2 yields.

For adsorbed moisture on plutonium oxide surfaces the radiation chemistry is not expected to be the same as liquid water especially for the interfacial molecules. Calcination of the oxide at 1223 K is effective in removing initially adsorbed water and other adsorbates and leads to the reduction of the specific area of the PuO_2 particles. Water molecules obviously can re-adsorb onto the actinide oxide surface and increasing the temperature leads to a higher desorption, thereby inhibiting effective energy transfer to adsorbed molecules [31]. With increases in the hydrogen pressures, the energy deposition in the gas phase will also increase; at a few atmospheres of pressure,

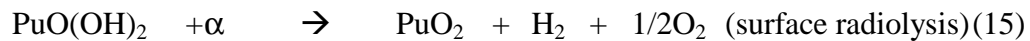
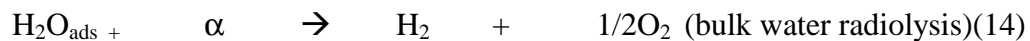
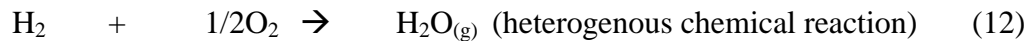
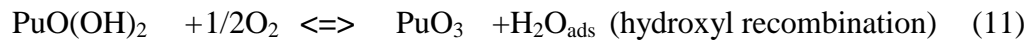
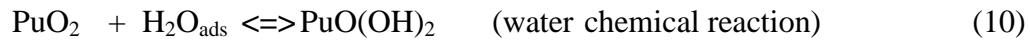
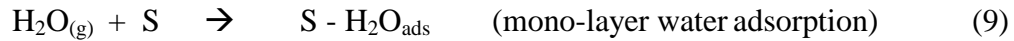
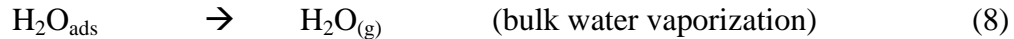
equilibrium between the rate of H₂ formation and water recombination would take place [23]. The higher the temperature, the higher the G (H₂) and the more rapidly the equilibrium is achieved. Radiolysis of air leads to the formation of nitrogen oxides, NO_x such as nitric oxide nitrogen dioxide and nitrous oxide [32]. If water vapor is present nitric acid can form and may lead to the oxidation of PuO₂ in storage containers [25,33]. The quantities of species formed will depend on the dose received [34]. For moist air systems the G (HNO₃) = 2.0 [33,34]. However, as mentioned earlier since NO₃⁻ act as scavengers, the molecular hydrogen production will be lower [20]. The formation of nitrogen oxides can account minor losses of oxygen over time in MIS Pu storage containers.

Particular attention is being devoted to adsorbed moisture on various metal oxide surfaces that are iso-structural with PuO₂ (e.g., CeO₂ or UO₂ or ZrO₂). By examining these substrates, the role of electronic structure in gas generation following radiolysis in the presence of water vapor will be determined. Secondary processes such as straggling particles and electron attachment processes are thought to also contribute to gas evolution through energy transfer and are also being investigated. Attempts are being made to predict the yields (G-values) of molecular species such as HO₂⁻, H₂O₂, H₂ and H₂O. The presence of impurities such as Br⁻, Cl⁻ etc., which act as scavengers and effect the yield of H₂ in the gas phase will also be considered in future experiments. The role that pre-hydrated electrons have in leading to molecular hydrogen production with helium ions is also currently being investigated. Pre-hydrated electrons are fairly mobile and are produced in solids due to energy loss processes by the passing radiation. Any electron that reaches the surface of the material and interacts with the water layer (or bulk water) can potentially produce molecular hydrogen. In simple terms, energy deposited anywhere in the system, and not just in the water layer, can lead to hydrogen formation. Simple micro-dosimetry calculations may lead to gross underestimates of molecular hydrogen formation. The "transfer" of energy from the solid phase to an absorbed layer has long been proposed to affect the production of gaseous products. The exact mechanism is not understood well enough to predict the outcome with Pu waste materials and remains a research priority. Chemical dosimetry studies in combination with exact particle counting studies will provide information on the importance of "transfer" processes. This field is largely unexplored and our work serves two very important functions. The first goal is to study the "transfer" processes (defined earlier) and the second goal is to understand the relationship between the particle size and average dose rate. If a PuO₂ particle radius exceeds the stopping distance of the α-particles, an increasing number of α-particles will be completely self-absorbed. Therefore, micro-dosimetry experiments need to be carried for various particle size distributions of PuO₂. Once the dose rate based on different size PuO₂ particles is determined, the stopping powers of water, salts, and other impurities (i.e. the radiation energy deposited per unit mass or radiation dose rate) can then be calculated. These experiments are being conducted at LANL using well-established dosimetry techniques.

These studies are designed to complement the studies being carried out at LANL on radiation-catalyzed gas phase reaction between hydrogen and oxygen and surface effects. This program will provide very valuable experimental data on radiolysis that are relevant to many important MIS programs such as the headspace gas analysis project and the ongoing shelf life studies project.

Modeling Gas Pressure and Stoichiometry

One of the primary goals of the integrated scientific study of water interactions at actinide and actinide oxide materials in storage containers is to develop a predictive tool that utilized to validate safe conditions over a significant time frame (20 years). To that end we have developed a modest computer program incorporating many of the physical, chemical, and radiolytic processes that have been described in previous sections of this paper. In addition, the modeling endeavor incorporates the physical characteristics of the 3013 transport container and includes properties of the contents (α -particle flux, surface areas of the actinide particles). The model in turn solves parametric rate equations to give gaseous, surface and condensed phase speciation. Throughout this process, measured and preferably published, rates of fundamental process (many of which have been described earlier) have been used. This model and its associated subroutines have been written in Visual Basic for Excel and readily run on conventional PC platforms. Although primitive at this early stage of development, the primary gas generation mechanisms have been delineated and are detailed in the following set of equations:



Where possible, identified rates and thermo-chemical parameters have been included from data sets identified in previous sections of this paper. The rate equations are iteratively solved and allowed to run for time interval representing several years of storage conditions. A representative modeling run is shown in Fig. 4 where gas phase water, oxygen from the packaging environment, and hydrogen gas

Gases

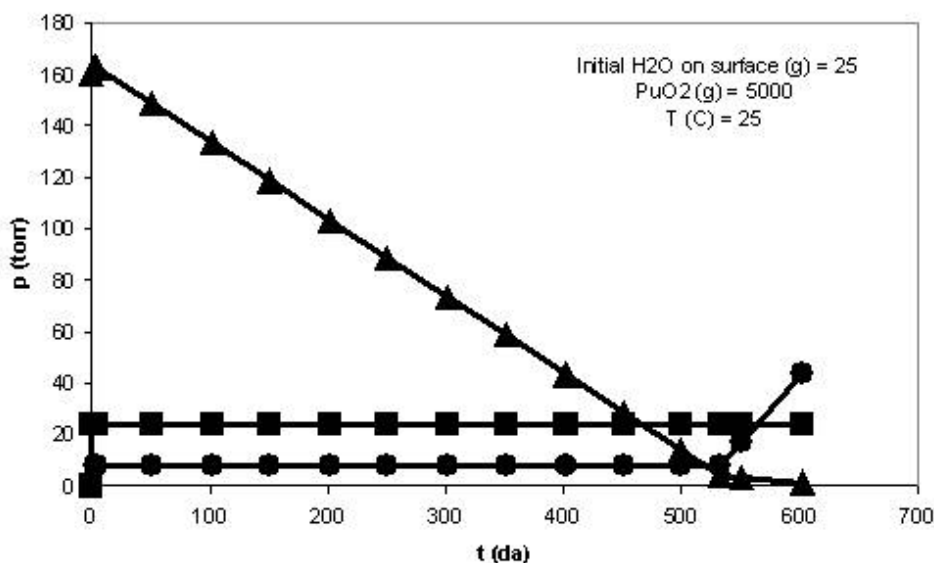


Fig. 4. Modeling results showing gas speciation as a function of time in days for an initial condition reflecting a typical 3013 storage scenario for initial conditions and selected reactions as described in text.

are monitored for ~ 600 days. The initial PuO₂ content reflects the maximum loading anticipated in a 3013 can and the initial water present in the system (25 grams) represents the maximum allowed on the calcined PuO₂ powder. Note that the initial oxygen concentration drops continually over the initial 500 days and that water rapidly attains an equilibrium pressure condition. Following the initial jump in concentration occurring in the first day, the H₂ concentration remains constant until the oxygen is depleted. At the point where the O₂ is depleted (500 plus days) the H₂ partial pressure rapidly rises. Although this example serves to illustrate the end result of many of the competing processes that account for creation and destruction of gas and condensed phase species, alteration of predicted outcomes can be assessed by incorporating new mechanisms and rates. This modeling effort will include new processes that have not been fully determined to date. A crucial validation of this modeling approach will occur when the first of many well-defined long-term storage tests produce data for direct comparison.

Summary

Resolved Issues

The corporate knowledge from shelf-life programs around the DOE/EM complex is that containers with known actinide oxide loadings do not show signs of extreme pressurization. The observation has been verified to date by LANL's Material Identification and Surveillance (MIS) project. The goal of the MIS project is to determine the chemical and physical character of stored materials, and to evaluate

processing needed to stabilize the materials in order to meet the 3013 standard. This program has examined 33 items representing a large fraction of the materials to be packaged for long-term storage. Extreme pressurization was not found in any of these items. In addition, appreciable amounts of H_2 and O_2 were not found to coexist in any of the surveillance containers [35].

With respect to the fundamental scientific research addressed in this paper, specific physico-chemical processes and transformations that have relevance to gas generation and storage of actinide materials have been identified and delineated. Additional chemical and physical processes and experiments have been designed to measure unknown or ill-determined thermochemical parameters. The mechanistic details and parameters have been utilized in developing mathematical models of gas generation of relevance to storage of actinide bearing materials. On the basis of preliminary modeling efforts the prediction of safe storage conditions based upon initial bounding conditions, processing steps, and known test case scenarios appears to be validated. Through incorporation of all the pertinent events likely to occur in well-defined actinide storage scenarios, safe bounding conditions of gas stoichiometry and pressure are expected to predominate (although not all processes and rates are completely understood).

Unresolved questions

For the PuO_2/H_2O corrosion reaction, areas of continued interest include the equilibrium behavior of the PuO_2/H_2O reaction, phase equilibria of the Pu-O system, the mechanism of water oxidation of the dioxide and metal, and thermodynamic, structural, and spectroscopic properties of PuO_{2+x} . Another essential aspect is the manner in which the reaction rate depends on the water concentration. Furthermore, does the existence of a hyper-stoichiometric oxide alter or significantly change the rates of other heterogeneous processes such as the $H_2 + O_2$ reaction? Ultimately, a complete understanding of the surface physics and chemistry of adsorbed water on actinide oxides is warranted and translates into a universally accepted G value for water adsorbed onto actinide oxides. All of these details need to be completely understood to confidentially model the kinetics of these reactions in a bounding storage scenario.

Future work on the H_2/O_2 recombination reaction needs to focus on the following areas: (1) further understanding of the kinetics and mechanism with pure dioxide, and (2) measurement of recombination rates over several other impure oxides. The data presented in this paper show that the measured recombination rates over the impure oxide were markedly slower than those for the pure oxide. This effect must be understood for various proto-typical oxides in order to successfully model this behavior. In addition, further work understanding the radiation chemistry of Pu and U + H_2O systems is being explored that assesses the relative role of dose actually received by plutonium and uranium oxides of varying particle size and surface area. Data from these experiments is of paramount importance because the new 3013 standard will be applied to materials with ~30 weight percent plutonium and with additional impurities expected to compromise some of these advantageous reactions. The obvious extension of the modeling effort is to accurately predict gas generation from more complex actinide oxide waste mixtures.

References

1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-term Storage," Department of Energy, DOE-STD-3013-96, September 1996.
2. "Assessment of Plutonium Storage Safety Issues at Department of Energy Facilities," US DOE Report DOE/DP/0123T, US Department of Energy, Washington, D.C., 1994.
3. J. Haschke, "Reactions of Plutonium and Uranium with Water: Kinetics and Potential Hazards," LA-13069-MS, December 1995.
4. J.L. Stakebake, D.T. Larson, and J. Haschke, *J. Alloys and Compounds*, 202, 1993, 251.
5. C. A. Colmenares, *Prog. Solid State Chem.*, 9, (1975), 139.
6. R.A. Van Konynenburg, D. H. Wood, R. H. Condit, and S. D. Shikany, "Bulging of Cans Containing Plutonium Residues: Summary Report," **UCRL-ID-125115**, Lawrence Livermore National Laboratory, Livermore, California, 1996.
7. P. Thiel and T. Madey, *Surface Sci. Reports*, 7 (1987) 211.
8. J. Stakebake, *J. Phys. Chem.*, 77 (1973) 581.
9. W.L. Manner, J.A. Lloyd, and M.T. Paffett, *J. Nucl. Mat.*, 275 (1999) 37-46.
10. M.T. Paffett, LANL, unpublished results 1999.
11. J.D. Farr, LANL, unpublished results 1999.
12. E. R. Gardner, T. L. Markin, and R. S. Street, *J. Inorg. Nucl. Chem.*, 27, (1965), 541.
13. J. M. Haschke and T. H. Allen, "Interactions of Plutonium Dioxide and Water and Oxygen-Hydrogen Mixtures," LA-13537-MS, January 1999.
14. J.A. LaVerne, Notre Dame University, Private Communication, 1999
15. B. Pastina and J.A. LaVerne, *J. Phys. Chem. A.*, 103 (1999) 1592.
16. K. Büppelmann, J. I. Kim, and Ch. Lierse, *Radiochim. Acta*, 44/45 (1988) 65.
17. J.Spinks, and R. J. Wood, *An Introduction to Radiation Chemistry*, John Wiley & Sons, Inc., New York, 1990.
18. D.J. Wronkiewicz, "Radionuclide Decay Effects on Waste Glass Corrosion" In: *Materials Research Society Symposium Proceedings, vol. 333. Scientific Basis for Nuclear Waste Management XVII*, A. Barkatt and R. A. V. Konynenburg, Eds., Materials Research Society, Pittsburgh, Pennsylvania, 83, 1994.
19. N.E. Bibler, *J. Phys. Chem.*, 79 (1975) 1991.
20. N.E. Bibler, *J. Phys. Chem.*, 78 (1974) 211.
21. W.G. Burns, and H. E. Sims, *J. Chem. Soc., Faraday Trans. 1*, 77 (981) 2803.
- 22 "TRUPACT II Safety Analysis Report for the TRUPACT-II Shipping Package (SARP)," **NRC Docket No. 9218**, 1994.
23. W.J. Gray and S. A. Simonson, "Gamma and Alpha Radiolysis of Salt Brines," **PNL-SA-12746**, Pacific Northwest Laboratory, Richland, Washington, 1984.
24. A.O. Allen, C. J. Hochanadel, J. A. Ghormley, and T. W. Davis, *J. Phys. Chem.*, 56 (1952) 575.
25. D.T. Reed, and R. A. Van Konynenburg, "Effect of Ionizing Radiation on Moist Air System," In: *Materials Research Society Symposium Proceedings, vol. 112. Scientific Basis for Nuclear Waste Management XI*, M. J. Apted and R. E. Westerman, Eds., Materials Research Society, Pittsburgh, Pennsylvania, 393, 1988.
26. "TRUPACT-II Safety Analysis Report, Attachments 1 and 2, Appendix 3.6.7. A1-1 and 3.6.8. Part 2.0, A2-1," (Rev. 1 May 1989).

27. J.M. Haschke and T. E. Ricketts, "Plutonium Dioxide Storage: Conditions for Preparation and Handling," **LA-12999-MS**, Los Alamos National Laboratory Report (1995).
28. R.E. Mason, T. Allen, L. Morales, N. Rink, R. Hagan, D. Fry, L. Foster, E. Wilson, C. Martinez, M. Valdez, F. Hampel, O. Peterson, J. Rubin, and K. Hollis, "Materials Identification and Surveillance: June 1999 Characterization Report," **LA-UR-99-3053**, Los Alamos National Laboratory, Los Alamos, New Mexico, 1999.
29. R.S. Dixon, *Radiat. Res. Rev.*, **2**, (1970) 237.
30. G.A.Kimmel, T. M. Orlando, C. Vezina, and L. Sanche, *J. Chem. Phys.*, 101 (1994) 3282.
31. A.A. Garibov, "Water Radiolysis in the Presence of Oxide," In: *Proceedings of the Fifth Tihany Symposium on Radiation Chemistry Held at Siofok 19-24 September 1982. Vol. 1, 2*, Hungary Akademiai Kiado, Budapest, 377, 1983.
32. S. Sunder, and N.H. Miller, *J. Nucl. Mater.*, 231(1996) 121.
33. J. Henshaw, "Modeling of Nitric Acid Production in the Advanced Cold Process Canister due to Irradiation on Moist Air," **SKB Technical Report 94-15**, AEA Technology, Decommissioning & Waste Management/Reactor Services, Harwell, UK, 1994.
34. R. May, D. Stinchcombe and H. P. White, "The Radiolytic Formation of Nitric Acid in Argon/Air/Water Systems," **AERE R 8176**, United Kingdom Atomic Energy Authority, Harwell Laboratory, Oxfordshire, UK, 1992.
35. R. Mason, T. Allen, P. G. Eller, R. Hagan, D. Horrell, and N. Rink, "Gas Generation in Pure and Impure Plutonium-Bearing Materials," *Transactions of the American Nuclear Society*, **81**, (1999), p. 104.