LA-UR 02- 4349

# The Essential Elements of Modeling Gas Generation From Well Defined Plutonium Materials

Mark T. Paffett
Los Alamos National Laboratory
Los Alamos, NM 87545, USA
505-665-2395
mtp@lanl.gov

Dan Kelly
Los Alamos National Laboratory
Los Alamos, NM 87545, USA
505-665-7388
dnkelly@lanl.gov

## Abstract

Processing of excess plutonium oxide (and related) materials intended for long-term storage is addressed in DOE standard 3013-2000. The essential elements addressed by this standard are eliminating or reducing to an acceptable level the entities that lead to gas evolution and consequent pressurization of the intended storage container system. Based upon the need to adequately understand and quantify these relevant parameters we briefly describe the current scientific knowledge of gas evolution from such systems. These associated research efforts have included fundamental kinetic and thermodynamic studies of water interactions at actinide oxide surfaces, radiolytic reactions of adsorbed water, interfacial reactions of hydrogen and oxygen, and radiolytic helium production. Utilizing, where possible, experimental parameters for many of the aforementioned processes we have developed a mathematical model with a minimum number of essential components that successfully models gas generation from well-defined $PuO_2$ materials with known amounts of deliberately added water. In this work we verify this model against real pressure versus time data (described at greater length in another manuscript in these conference proceedings) and subsequently assure the safety envelope of design criteria for both short- and long-term storage and transportation of these material classes. These modeling results predict pressures and gas phase mole fractions over well-defined DOE 3013 container test cases well in advance of actual long-term surveillance information and provide confidence in safe storage of plutonium oxide material classes.

## 1. Introduction and Background

The potential for radiolytic gas generation leading to container pressurization is a major issue affecting the ability of the Department of Energy Environmental Management Program (USDOE-EM) to transport and secure for long-term storage nuclear materials for possible further disposition. The current ability to predict sealed container pressures and gas-phase compositions is restricted by a limited, finite understanding of the fundamental processes that contribute to gas generation. For plutonium bearing materials this conservatism in gas pressurization is embodied in Appendix B of the DOE 3013-2000 Standard "Stabilization, Packaging, and Storage of Plutonium Bearing Materials (**1**)." In this cited appendix, approximations and simple mathematical equations are derived that lead to an extreme conservatism for allowed moisture content in actinide oxide materials and consequently, increased costs for materials management of low moisture content materials. In spite of this simple mathematical description contained in Appendix B of DOE 3013-2000 that predicts substantial gas pressures, actual surveillance data for fairly well defined plutonium bearing materials with known moisture contents has revealed small to negligible pressure changes. This inconsistency between the mathematical description that dictates processing, storage, and transportation scenarios and the observed real world surveillance data for these well-defined plutonium bearing materials has lead to frequent, costly delays and considerable additional testing. In addition, the lack of a reliable and validated modeling procedure suggests a critical need based upon this disconnect between observed and predicted behaviors.

In this manuscript, we present modeling results that are directly compared against real world gas pressurization versus time data for well-defined $PuO_2$ solids with deliberately added water contents ranging from 0.5 to 2.0 weight percent at room temperature. This mathematical model describing pressure versus time is a significant extension of previous simpler modeling efforts that incorporate only gas phase reaction chemistry or only radiation derived modeling efforts such as employed by RadCalc (**2**). Embodied in the mathematical model of this work are the thermodynamics and kinetics of water adsorbing and desorbing from $PuO_2$, radiolysis of adsorbed water in a variety of physically plausible scenarios, and hydrogen and oxygen recombination reactions. Additional reaction rates for the suggested water and oxygen-assisted corrosion of $PuO_2$ to form hyper-stoichiometric $PuO_{2+x}$ can also be added. In practice it is possible to mathematically model observed behavior using the limited set of reactions mentioned above for short time intervals applicable to transportation scenarios. Furthermore, the predicted gas pressure increases for materials stored at room temperature are significantly below that predicted on the basis of Appendix B of DOE 3013-2000 and suggest increases in allowable moisture content are possible for room temperature plutonium bearing material storage. In addition, extensions to more complex waste forms and longer time increments are envisioned.

## II. EXPERIMENTAL DATA AND RELATIONSHIP TO MODELING EFFORT

A number of previous experimental studies have attempted to address gas generation arising from moisture initially present on well-characterized, moderately pure plutonium dioxide samples. Much of this data has been briefly captured in a recent report [**3**] issued at Los Alamos National Laboratory and discussed in the context of how best to utilize this knowledge from a predictive standpoint. Although not explicitly stated, much of the data cited in the report is plagued by experimental difficulties and the simple fact that the span of initial moisture contents runs from 0.00007 only up to 0.58 weight percent. In addition, and in spite of this limited variability in initial moisture content, very little gas pressurization is observed to occur. In fact, most sealed containers under examination show a marked loss of pressure and anomalous gas phase composition changes. In light of these incomplete data sets, additional research conducted at Savannah River Technology Center (SRTC) has recently become available and includes a series of short duration studies monitoring gas pressure and composition changes occurring over well-characterized plutonium dioxide (prepared from oxalate precipitation followed by calcinations) stored with deliberately added water in an air environment. The specific details regarding preparation and gas pressure and composition determinations are contained in a companion paper in this symposium series [**4**]. In the following portions of the document we attempt to model and predict gas phase pressure changes and compositional changes contained in these data sets.

The selected SRTC data of Livingston and Duffey [**4**] is shown in Fig 1. and contains gas pressure changes as a function of time for material calcined to 700 C for different initial water loadings. Programmatic reasons for examining higher initial water contents than specified in the DOE 3013-200 standard include supporting a technical basis for easier quantification of moisture content with higher precision and accuracy, and the obvious desire to observe accelerated gas pressurization changes that are clearly not present for low moisture content materials mentioned in Ref 1.

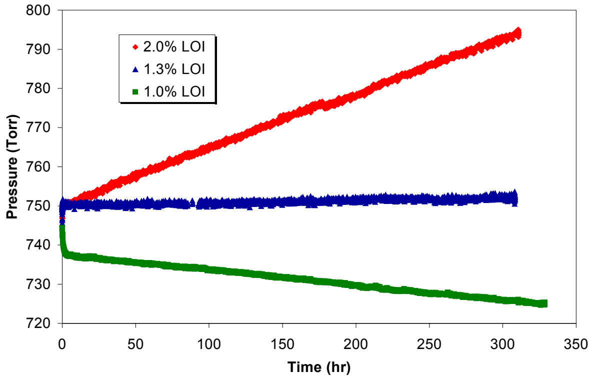

Figure 1 Gas Pressure as a Function of Initial Water Loading for $PuO_2$ (other details supplied in text)

## III. DEVELOPMENT OF MATHEMATICAL MODEL AND DESCRIPTION

Our model has been developed using Chemkin (5) software (Reaction Design). Chemkin provides a modular format where chemical equations describing heterogeneous reaction mechanisms are evaluated and subsequently linked to an application program. We are evaluating the chemistry occurring in sealed canisters using the Aurora application module, which simulates a constant stirred tank reactor. The Aurora application module is run in a closed-system transient mode to determine canister pressure and gas-phase mole fractions as a function of time.

For the purposes of modeling the data of Fig. 1, we employ the following simplistic gas-generation scheme. On the oxide surface, adsorbed hydroxyls undergo radiolytic decomposition to form gas-phase hydrogen and oxygen,

$$PuO(OH)_2 \rightarrow PuO_2(O) + H_2\text{, with } k_{H2} \qquad (1)$$

$$PuO_2(O) \rightarrow PuO_2 + ½\, O_2\text{, with } k_{O2} \qquad (2)$$

where the *k*'s are rate coefficients for the radiolytic reactions. In subsequent (bulk) water layers these reactions are modeled similarly,

$$S(H_2O) \rightarrow S(O) + H_2\text{, with } k_{H2,i} \qquad (3)$$

$$S(O) \rightarrow S + ½\, O_2\text{, with } k_{O2,i} \qquad (4)$$

where S can be thought of as an adsorption site within a layer of water on the oxide surface. Again, *k*'s are rate coefficients for the radiolytic gas production reactions, where the subscript *i* refers to the number of the water layer above the oxide surface, as explained more fully below. Additionally, gas-phase hydrogen and oxygen may recombine to form water through a surface-mediated process as follows.

$$S + H_2 + ½\, O_2 \rightarrow S(H_2O)\text{, with } k_{recom} \qquad (5)$$

While it is often thought that only hydrogen (and not oxygen) will be evolved into the gas phase from the radiolysis of adsorbed water, recent experimental evidence has shown that oxygen is evolved and increases in concentration when there is a sufficient quantity of water present (ca. several wt. %) (4). Oxygen is also released to the gas phase when monolayer (ML) coverages of water on crystalline $UO_2$ are exposed to a low energy electron source under ultra high vacuum conditions, effectively simulating a radiolysis field (6). In spite of the trivial nature of the mechanism contained in equations 1-5, it provides a means of independently controlling the rates of formation of $H_2$ and $O_2$ and the rate of water recombination as functions of water loading. We recognize that the radiolysis of water on a molecular scale is mechanistically quite complex (7) and involves many intermediates, such as peroxides that would be necessary for the facilitation of an oxygen producing mechanism in bulk water radiolysis. We also note that while the surface chemistry occurring on $PuO_2$ is rather extensive and is not well understood and controversial. equations 1-5 are sufficient for an initial attempt at describing experimental results of canister pressurization. Also, we are aware that radiolysis of gas-phase constituents may lead to recombination of hydrogen and oxygen to form water (7), however, we believe the rate of chemical recombination (undoubtedly through a surface-mediated mechanism not detailed here) is significantly faster (8). These modeling mechanisms require refinement and modification to reflect continuing experimental and theoretical investigations of the reactions they describe.

Values for the rate coefficients of equations 1-5 are input on a molar basis to evaluate overall reaction rates. Chemkin solves the heterogeneous reaction equations and evaluates overall reaction rates according to a concentration-dependent expression. For example, the rate of radiolysis of adsorbed hydroxyls to form surface bound oxygen atoms and gas-phase hydrogen shown in equation 1 is given by

$$R = k * \rho * SA * [PuO(OH)_2], \qquad (6)$$

where R is the rate of hydrogen production in moles/sec, $\rho$ is the $PuO_2$ surface site density (moles/cm$^2$), SA is the total $PuO_2$ site area (cm$^2$), and $[PuO(OH)_2]$ is the concentration, or fractional coverage, of adsorbed hydroxyls. It should be noted that all of the above reaction equations are evaluated as pseudo-first order reactions, and the reaction rates are simply dependent on the concentration of reactant species.

Other pertinent simulation parameters and methodology are as follows. The canister from which data in Figure 1 is obtained contains 9 g $PuO_2$ (7.94 g Pu-239) and has a free volume of 25 ml. A surface area of 5 m$^2$/g is assumed for the $PuO_2$ powder. Assuming a site area for water adsorption of 10.5 Å$^2$, we note that 1 wt. % $H_2O$ corresponds to a surface coverage of 7 ML of $H_2O$ on 9 g of $PuO_2$. In all cases the canister is packaged with dry air (21 % $O_2$, 79 % $N_2$) at 300 K and 1 atmosphere.

Chemkin model development allows for chemical reaction rates that are dependent on water loading. Since relatively small mass loadings of water equate to multiple layers of adsorbed water on $PuO_2$, the ability to incorporate concentration-dependent water reactions into the model may be paramount to properly describing the overall system behavior. Specifically, experimental evidence suggests that the radiolysis rate coefficients for adsorbed water are dependent on the proximity of the water to the radiolytic source (9). Hence, proper description of the behavior for a 1 wt. % water loading may require the rate coefficient of water radiolysis of the seventh ML to be substantially different than that of first ML water directly bound to the $PuO_2$ surface. This methodology of correlating the mass of water loaded to a layered simulation structure where the kinetic parameters describing water reactions are layer-dependent is referred to several times below and the layer-dependent radiolysis rates are delineated where necessary. Figure 2 shows a schematic corresponding to the loading of 2 wt. %, or 14 ML, of $H_2O$ by this layered approach. We have chosen to break up the total water content into four separate components, each of which may have independent rate coefficients. In this case equations 1 and 2 apply to the first ML of water, with $k_{H2}$ and $k_{O2}$. Equations 3 and 4 apply to the second ML of water, with $k_{H2,2}$ and $k_{O2,2}$, to the

Figure 2. Two weight percent (14 monolayers, ML) water loaded on $PuO_2$ within four distinct layers. The amount of water loaded is not equivalent on each layer, and the chemistry of each layer can be independently controlled.

third and fourth MLs of water, with $k_{H2,3}$ and $k_{O2,3}$, and to the remaining water (> 4 ML), with $k_{H2,4}$ and $k_{O2,4}$. In principle the layers can hold arbitrary amounts of water and each layer can have independent kinetics.

An estimate of the initial rate of hydrogen evolution due to water radiolysis may be obtained using RadCalc software (10). RadCalc predicts a rate of hydrogen production of approximately 2.5 x $10^{-11}$ moles/sec, using an input of 9 g $PuO_2$ (designated as pure Pu-239) and 90 mg, or 1 wt. %, water. For the surface area and site density used to depict 9 g $PuO_2$ in the Chemkin model, a rate coefficient of 5 x $10^{-9}$ $sec^{-1}$ gives an initial gas generation rate of 2.5 x $10^{-11}$ moles $H_2$/sec arising from the radiolysis of 90 mg of adsorbed water. RadCalc does not conserve mass and hence predicts a constant rate of $H_2$ production with time, no matter what fraction of the initially loaded water is extant in the system as time passes. Chemkin recognizes that as the radiolysis of water proceeds, the rate of hydrogen production must decrease because the concentration of water diminishes.

The rate coefficient of 5 x $10^{-9}$ $sec^{-1}$ for hydrogen production can be taken as the value corresponding to bulk water radiolysis. When discussing water adsorbed on the surfaces of radioactive materials, a pertinent question is how this rate coefficient may vary from that expected for bulk water. One viewpoint is that $k_{H2,i}$ should decrease as successive layers of water are loaded on the surface because each layer of water is farther away from the radiolytic source. A second viewpoint is that adsorbed hydroxyls do not undergo radiolysis, and hence $k_{H2} = 0$, but that $k_{H2,i}$ increases from 0 to the bulk radiolysis rate as successive amounts of water are loaded. Figure 3 shows the pressurization of a 25 ml canister packaged with 9 g $PuO_2$ and both 0.5 and 2 wt. % water, using these different scenarios for the variation of $k_{H2}$ as a function of $i$ (see table 1). Note that in Figure 3 only equations 1 and 3 are operative, there is no oxygen production or $H_2/O_2$ recombination. The top trace of Figure 3 is the case where all water behaves identically and undergoes radiolysis at rate corresponding to that of bulk water. For a 2 wt. % water loading the pressurization is greater for the $k$-increasing case than for the $k$-decreasing case, while the reverse is true for a 0.5 wt. % loading. This is expected since in our layering approach of Figure 2 only ~ 0.25 wt. % water is located in layers 1 and 2, ~ 0.25 wt. % in layer 3, and almost 1.5 wt. % in layer 4. Small amounts of water imply that $k_{H2}$, $k_{H2,2}$ dominate

| $k_{H2}$ (units of $10^{-9}$ $sec^{-1}$) | | |
|---|---|---|
| Layer | $k$ increasing | $k$ decreasing |
| 1 | 0 | 5 |
| 2 | 1.25 | 2.5 |
| 3 | 2.5 | 1.25 |
| 4 | 5 | 0.63 |

Table 1: Rate coefficients for hydrogen production from the radiolysis of water layers.

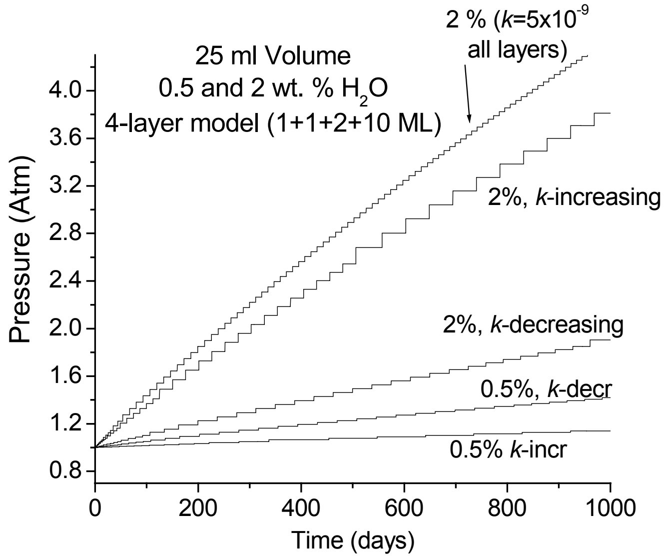

Figure 3. Canister pressurization with variation of $k_{H2}$ (as given by Table 1) under water loadings of 2 and 0.5 wt. %.

while large amounts of water imply that $k_{H2,4}$ dominates, i.e., the kinetics of layer 4 will dominate so long as sufficient amounts of water are loaded to populate this layer. There is much experimental controversy regarding radiolysis rates for first layer hydroxyls or near surface water. (Examination of the gas generation rates in the Livingston and Duffey data for low water content $PuO_2$ materials implies that the first layer and/or hydroxyl covered $PuO_2$ rates of radiolytic decomposition are orders of magnitude slower than for multi-layer and or bulk water radiolysis). An attractive feature of the modeling format employed here is radiolysis rates can be easily modified and employed vs. water loading as new results emerge from collaborative experimental programs.

In attempting to model the pressure curves and final gas-phase mole fractions of $H_2$ and $O_2$ (not shown) of Figure 1 equations 1-5 are used. It should be noted that while the gas-phase mole fractions are not shown in Figure 1, the 2 wt. % water data set exhibited a net increase in oxygen over time, while the other data sets showed net decreases in oxygen concentration over time. In fitting the results of Figure 1, a layered approach was not employed, but rather all water was treated equivalently thus limiting the number of parameters available for achieving a fit. Here, hydrogen production through the radiolysis of water was given a rate coefficient of $5 \times 10^{-9}$ $sec^{-1}$. Rate coefficients for oxygen production, $k_{O2}$ for equations 2 and 4, and for the recombination of hydrogen and oxygen to reform water, $k_{recom}$ for equation 5, were determined simultaneously by fitting the pressure curve and final $H_2$ and $O_2$ mole fractions for the 1 wt. % water loading data set. A rate coefficient for oxygen production, $k_{O2}$, of $8.5 \times 10^{-7}$ $sec^{-1}$ was found in this fashion, and this number was assumed not to change with water loading. The $H_2/O_2$ recombination rate coefficient, $k_{recom}$, was found to be $5 \times 10^2$ $sec^{-1}$. We note that the rate coefficient for reformation of water determined in this fashion is much higher than that which would be expected from radiolysis of gas-phase $H_2$ and $O_2$, indicating that a surface mediated chemical recombination is most likely responsible for the reformation of water. Likewise, we found it impossible to fit all three data sets using constant values for $k_{H2}$, $k_{O2}$, and $k_{recom}$. Hence we fit the 2 wt. % data set by varying $k_{recom}$ to achieve the proper pressure curve (while keeping $k_{O2}$ constant). At 2 wt. % water a $k_{recom}$ of $5 \times 10^{-2}$ $sec^{-1}$ was found, and the final gas-phase mole fractions were reasonably close to experimental values, indicating a constant $k_{O2}$ suffices. Note that to achieve a reasonable fit to the experimental pressure curves, the rate coefficient for water reformation must vary over four orders of magnitude while the water loading only increases 1 wt. %. This implies (as expected) a very strong inhibition effect by adsorbed water on the recombination kinetics of $H_2$ and $O_2$. Lastly, we interpolated $k_{recom}$ with water loading to find a $k_{recom}$ of $3.5 \times 10^2$ sec-1 at 1.3 wt. % water and then input this parameter to model the remaining data set. The modeled fit shows a slight pressure decrease while the experimental data shows an effectively flat pressure curve. The results of these endeavors are shown in Figure 4.

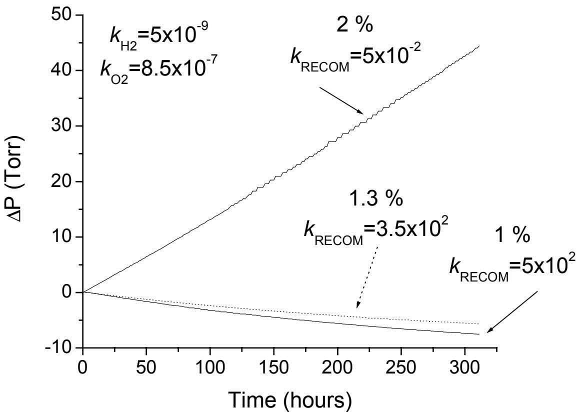

Figure 4: Modeling results and rate coefficients for the experimental data of Fig. 1.

## IV. SUMMARY

In comparing experimental results contained in the work of Livingston and Duffey with our modeling endeavor we note that the very strong non-linear behavior with respect to gas generation and gas phase composition requires a strongly non-linear mathematical approach to achieve a satisfactory fit.. This result also implies that a simple algebraic expression, as contained in Appendix of the DOE 3013-200 Standard, will never sufficiently account for observed behaviors over Pu bearing solids containing moisture. Gas generation behavior from more complex, impure Pu bearing mixtures will be less accurately described by simple algebraic expressions. Reasonable attempts to fit observed behavior over well-defined $PuO_2$ powders inevitably require a highly non-linear kinetic rate expression for $H_2$ and $O_2$ recombination that includes a significant inhibition effect by adsorbed water. Finally, although we do not address the molecular level detail of separate $H_2$ and $O_2$ radiolysis rates they are noted to present in the data of References 3 and 4.

## ACKNOWLEDGEMENTS

Primary support for this investigation was made possible through funding provided by the Nuclear Materials Stabilization Program Office, United States Department of Energy, Albuquerque Operations and Headquarters Offices, under the auspices of the DNFSB 94-1 Research and Development Project**.**

## REFERENCES

1. DOE Standard 3013-2000, “Stabilization, Packaging and Storage of Plutonium Bearing Materials”, US Dept. of Energy. 2000.
2. J. G. McFadden, Radcalc for Windows Version 2.01, Volume 1: User’s Manual, HNF-2549, Rev. 0, 1995.
3. G. Bailey, E. Bluhm, J. Lyman, R. Mason, M. Paffett, G. Polansky, G.D. Roberson, M. Sherman, K. Veirs, and L. Worl, “Gas Generation from Actinide Oxide Materials”, Los Alamos Report LA-13781-MS, December 2000, Los Alamos NM 875454.
4. R. Livingston and J. Duffey, paper presented at this symposium.
5. R. J. Kee, *et. al.*, *Chemkin Collection*, Release 3.6, Reaction Design, Inc., San Diego, CA, 2000.
6. S. A. Joyce, (private communication).
7. J. Spinks and R. J. Wood, *An Introduction to Radiation Chemistry,* John Wiley & Sons, Inc., New York, 1990.
8. L. A. Morales, “Preliminary Report on the Recombination Rates of Hydrogen and Oxygen over Pure and Impure Plutonium Oxides,” Report LA-UR-98-5200, Los Alamos National Laboratory, Los Alamos, NM, 1998.
9. J. A. LaVerne and L. Tandon, J. Phys. Chem. A, submitted.
10. J. G. McFadden, Radcalc for Windows Version 2.01, Volume 1: User’s Manual, HNF-2549, Rev. 0, 1995.