Report on the modeling of the large MIS cans

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Abstract:

Changes in gas composition and gas pressure for closed systems containing plutonium dioxide and water are studied using a model that incorporates both radiolysis and chemical reactions. The model is used to investigate the behavior of material stored in storage containers conforming to DOE-STD-3013-99 storage standard. Scaling of the container to allow use of smaller amounts of nuclear material in experiments designed to bound the behavior of all material destined for long-term storage is studied. It is found that the container volume must be scaled along with the amount of material to achieve applicable results.

Introduction:

In accordance with non-proliferation concepts, the United States plans to store excess weapons-grade plutonium until an ultimate disposition path can be finalized. Most of this excess plutonium will be stored as stabilized plutonium oxide, since PuO_2 is thought to be thermodynamically stable under storage conditions. Plutonium dioxide is known to absorb small amounts of water, and the radiolysis of water to form hydrogen gas is considered to be the greatest concern for safe long-term storage. Recently, the chemical reaction of water with PuO_2 to form a hyper-stoichiometric oxide PuO_{2+x}, has been found.[7]

The effects of temperature (T), surface area (SA), scaling, initial atmosphere, and water content on the evolution of the gas composition and pressure of 3013-99 storage containers to 1500 days are investigated. The storage standard limits the amount of water to less than 0.5 weight percent. These materials potentially have a wide range of surface areas and the number of equivalent water monolayers for 0.5 weight percent can range from less than one full monolayer to more than 20. Experimental results indicate that for radiolysis the first monolayer is not reactive whereas the higher equivalent monolayers tend to act like liquid water, which generates H_2, O_2, and oxidizers (i.e. H_2O_2). In order to reproduce experimental results, the first monolayer of water is not radiolytically reactive in the model.

Computational:

The model we use, which we refer to as Lyman 35, was developed as an Excel spreadsheet[8] Assumptions in the model are:

- PuO_2 is pure since the model hasn't been adapted to calculate the effects of impurities.

- The surface of PuO_2 has a top layer of oxygen. A valid assumption since uncoordinatedly saturated atoms of plutonium would be very reactive.
- All of the containers have been sealed properly and are air-tight.
- Temperature regulation is precise and accurate.

This model includes thermodynamics of radiolysis, and chemical reactions, Table 1 (listed below). This system is described by using the Arrhenius equation, eq. 1. Activation energies, E_a, are listed in Table 1. The temperature is T. The idea gas constant, R, is 8.31441 J K^{-1} mol^{-1}. Preexponential factors, A, were experimentally determined, Table 1. The model uses small time steps and a visual basic for applications script to get a self-consistent field for the coupled reactions listed in Table 1.

$$K = A \cdot e^{E_a/RT} \qquad \text{Eq. 1}$$

The volume of the head space is calculated via the DOE-STD-3013 appendix B guide, eq. 2.

$$V_g = V_t - \frac{M_{PuO_2}(g)}{\rho} \qquad \text{Eq. 2}$$

Results and Discussion:

Our interest is in the behavior of material stored in existing storage containers, which have an internal volume of 2.667 L and may contain up to 5 kg of material. Experimentally, the full-scale container is problematic, both from the amount of material that must be handled and the amount of space required to study many systems. Previous studies used a container with an average volume of 52.5 cm^3 with 10 g of material, which does not linearly scale to the existing storage containers. New experiments planned at Los Alamos National Lab (LANL) will use containers scaled (1/500) to the existing storage containers with an internal volume of 4.5 cm^3 and 10 g of material (MIS surveillance can). Therefore, in these models we use these three volumes (2.667 L, 52.5 cm^3, and 4.5 cm^3) and material masses (5 kg, 10 g, and 10 g), in order to compare results for the three systems.

There is one set of experimental data available in which the gas composition and overall pressure has been followed over time.[5] This model reproduces the experimental pressures[5] to within a factor of 1.5 and predicts the overall trends for hydrogen. While the small list of reactions in Table 1 does not include all the chemistry that is available inside the can, it tends to reproduce the gross

M^a	Reaction	A	E_a
R	$PuO(OH)_2 \rightarrow PuO_2 + ½ H_2(g) + ½ H_2O_2(s)$	$1.56 \cdot 10^{-8}$	0
R	$H_2(g) + ½ O_2(g) \rightarrow H_2O(g)$	$2.83 \cdot 10^{-6}$	0
R	$H_2O(s) \rightarrow ½ H_2(g) + ½ H_2O_2(s)$	$1.56 \cdot 10^{-8}$	0
R	$H_2O_2(s) \rightarrow H_2O(g) + ½ O_2$	$1.4 \cdot 10^{-8}$	0
C	$H_2O(s) \rightarrow H_2O(g)$	$1.32 \cdot 10^{7}$	$4.4 \cdot 10^{4}$
C	$H_2O(g) + S \rightarrow H_2O(s) \cdot S$	0.632	0
C	$PuO_2 + H_2O(s) \rightarrow PuO(OH)_2$	$8.1 \cdot 10^{-4}$	0
C	$PuO(OH)_2 \rightarrow PuO_2 + H_2O(s)$	$5.6 \cdot 10^{-1}$	$1.3 \cdot 10^{5}$
C	$PuO(OH)_2 + ½ O_2 \rightarrow PuO_2(OH)_2(s)$	$1.4 \cdot 10^{-4}$	$3.9 \cdot 10^{4}$
C	$PuO_3 + H_2(g) \rightarrow PuO(OH)_2(s)$	$2.7 \cdot 10^{-8}$	0
C	$H_2(g) + ½ O_2(g) \rightarrow H_2O(g)$	$5.9 \cdot 10^{-6}$	0
C	$PuO(OH)_2 + H_2O_2(s) \rightarrow PuO_2(OH)_2 + H_2O(s)$	$1.35 \cdot 10^{-4}$	$3.9 \cdot 10^{4}$

Table 1 Reactions of Lyman's model 35. a) M is the mechanism C)hemical or R)adiolysis

experimental results. Some of the thermodynamics are estimated because experimental values are not available. Better values will lead to better models. Also, more reactions, will lead to a better model.

We created nine models to investigate the effects of temperature, surface area, scaling, initial atmosphere, and water content on the evolution of the gas composition and pressure within the three containers to 1500 days. In order to estimate the headspace gas volume (V_g) a relationship between the container volume (V_t) and the material mass is

needed. Initially, Lyman 35 used $V_g=V_t \cdot 0.4$ instead of Eq. 2. The effect of the two approaches are being compared to elucidate the effect of V_g on the results. This will become important in future work when the model is extended to include less dense impurities.

For model 1, a standard MIS surveillance can of 4.5 cm^3 was chosen with a V_g of 0.0018 L. We added 10 g of PuO_2 and 0.1 weight percent of water. Temperature was set to 315 K. The initial pressure inside the can was set to 600 torr of N_2, and 160 torr of O_2. The surface area of the oxide was set to 1 m^2/g. The result of the modeling predicts a maximum pressure of 2.93 bar (42.50 psia). The O_2 is completely consumed after ~117 days of storage and H_2 production starts after 117 days, becoming $1.4 \cdot 10^{-4}$ moles within 1500 days.

In model 2, the surface area changed from 1 m^2/g to 5 m^2/g and retained all of the other parameters. The pressure did not increase to significant levels because the increased SA resulted in less than one monolayer being formed.. Since all of the water was used in the construction of the monolayer, no "liquid-like" water was available to make H_2 and pressurize the canister.

In model 3 all the parameters remain the same as in model 1, except we calculate the V_g using eq 2, to get 0.0036 L for V_g. Hydrogen behaves as an ideal gas in the pressure and temperature regimes that we are interested in this paper. Model 3 predicts a maximum pressure of 1.75 bar (25.38 psia) inside 1500 days, mainly because there is more headspace volume to expand the generated gas into.

In order to compare reults from the MIS surveillance can to existing experimental data in which V_t = 52.5 cm^3, we created model 4. Model 4 has the same parameters as model 3 except the volume is 11.67 times larger (52.5 cm^3 versus 4.5 cm^3). Model 4 predicts a reduction in the maximum pressure to 1.08 bar (15.95 psia), as expected due to the increased volume for the generated gas to expand into.

In order to examine the effects of increasing pressure inside the canister, we increased the amount of water. Using model 3, but increasing the water to 0.5 weight percent we created model 5. The pressure curve is very similar to models 1 and 3, in that the pressure rises quickly at first due to the evaporation of water. Then the O_2 is used up so water can not be regenerated inside the model, and the pressure increases due to H_2 generation to a maximum of 6.38 bar (92.53 psia) inside 1500 days due mostly to H_2 generation. Model 5 has similar chemical reactions to model 3. The higher final pressure is due to a combination of the available oxygen being used up more rapidly, in 55 days for model 5 as compared to 277 days in model 3, and more rapid H_2 generation because more liquid-like water is available.

The large can studies were carried out using the same methodologies as detailed in the aforementioned small can analysis. V_t was set to 2.6666 L, V_g was calculated via eq. 2 to be 2.2319 L. The temperature was set to 315 K. Twenty-five grams of water were added to 5000 grams of pure PuO_2 (0.5 weight percent water). Six hundred torr of nitrogen and 160 torr of oxygen were also added to the

system. The surface area was set to 5 m^2/g. The simulation was run out to 1500 days, to create model 6.

The system starts at 1 bar and increases to 1.12 bar as the water evaporates. At 71 days, the oxygen is all used up and hydrogen production starts. Model 6 reaches a maximum pressure of 3.88 bar (56.27 psia) in 1500 days.

Model 7 was created by using all of the parameters from model 6 except for the V_g approximation. The head space of the 3013 type storage container was computed using $V_g = V_t \cdot 0.4$ calculation ($V_g = 1.067$ L). Model 7 had a maximum pressure within 1500 days, of 7.45 bar (108 psia).

The first parameter that we would like to discuss is surface area. In Table 2, model 1 and model 2 are compared. In model one, the oxygen is used up in 117 days and the final pressure of the storage container after 1500 days is 2.93 bar. In model two, the pressure did not increase to significant levels inside 1500 days. The reason behind this is that in model 2, there was only enough water to form 1.07 monolayers, in model 1 there was enough to form 5.3 monolayers of water.

Since that the first monolayer is assumed to be nonreactive (as found by Livingston[3]), the chemistries are different.

model	V_g	V_g (cm^3)	Initial atmosphere	SA (m^2/g)	P$_{max}$ (bar)
1	$V_g = 0.4 \cdot V_t$	4.5	Air	1	2.93
2	$V_g = 0.4 \cdot V_t$	4.5	Air	5	1

Table 2: Models 1 and 2 compared. The effect of Surface Area.

Secondly, we would like to discuss the effect of water. The only difference in models 3 and 5 is that model 3 has 0.1 weight percent water, and model 5 has 0.5 weight percent water, and model 5 has larger surface area, the models have the same starting conditions, Table 3. In model 3, the final pressure inside 1500 days was 1.75 bar. In model 5, the final pressure inside 1500 days was 6.38 bar. But due to the surface area being different, we can not directly compare them. We can only conclude that with more water, comes more pressure, and higher surface area uses more water to form the first monolayer which is nonreactive in this model. To directly compare these systems, model 5 was reran with a surface area of 1 m^2/g (all of the other parameters were kept the same), making model 5a, to ensure only the effect of water is compared. The final maximum pressure inside 1500 days was 8.71 bar. Therefore, pressure increases faster than linearly with water if all the other parameters are the same.

Model	V_g	V_g (cm^3)	Initial atmosphere	SA (m^2/g)	P$_{max}$ (bar)
3	Eq. 2	4.5	air	1	1.75
5	Eq. 2	4.5	air	5	6.38
5a	Eq. 2	4.5	air	1	8.71

Table 3: Models 3, 5, and 5a compared. The effect of adding water.

Our third point is the effect of scaling the volume, with all of the reagents scaled by a constant amount, i.e. linearly scaling. This is shown in Table 4, where we compare models 3 and 6 and models 1 and 7. Model 3 had a final maximum pressure of 1.75 bar inside 1500 days. Model 6 had a final maximum pressure of 3.88 bar inside 1500 days. Model 1 has a final maximum pressure of 2.93 bar inside 1500 days. Model 7 had a final maximum pressure of 7.45 bar inside 1500 days. The difference in pressures between model 1 and model 7 can be explained by surface area. To directly compare these systems, model 7a, was constructed using $V_t = 2.666$ L, $V_g = V_t \cdot 0.4$, 5000 g of PuO$_2$, and 0.1 weight percent water, 315 K, in air for 1500 days, and the maximum final pressure of model 7a was 2.45 bar. This is very close to model 1's maximum final pressure of 2.93 bar. (The error can be attributed to small round-off errors in each interaction in the summing routine). The same treatment was computed for models 3 and 6. Since 6 has five times the surface area and five times the water of model 3, model 6a was constructed. Model 6a is identical to model 6 except the surface area is 1 m^2/g. The final pressure for model 6a was 1.48 bar. The final pressure for model 3 was 1.75 bar. Again the error, is due to round-off's in the summing routine. In the same way, the results of bench-scale experiments can be used to predict the behavior in larger cans using linear scaling of the volume and mass, since the chemistry is the same (as predicted by the model).

Model	V_g	V_g (cm^3)	Initial atm.	SA (m^2/g)	P$_{max}$ (bar)
3	Eq. 2	4.5	air	1	1.75
6	Eq. 2	2666	air	5	3.88
6a	Eq. 2	2666	Air	1	1.48
1	$V_g = 0.4 \cdot V_t$	4.5	air	1	2.93
7	$V_g = 0.4 \cdot V_t$	2666	air	5	7.45
7a	$V_g = 0.4 \cdot V_t$	2666	air	1	2.45

Table 4: Models 3 and 6 and models 1 and 7 compared. The effect of linear scaling.

Our fourth point is the effect of scaling of different reagents differently, i.e. nonlinear scaling. Model 4 has 0.1 weight percent water, and model 5 has 0.5 weight percent water, Table 5. Also model 4 has 11.67 times the amount of O$_2$ as compared to model 5. Model 4 reaches a maximum final pressure of 1.1 bar. Model 5 reaches a final maximum pressure of 6.38 bar, due to five times the water available. This inequality of pressure is due to more oxygen in model 4 than in model 5 and pressurization of the storage container can not start until all of the oxygen has been consumed. The 0.1 bar pressuration is due to the vapor pressure of water. To directly compare the two systems, model 5a was constructed which is identical to model 5, but has a 0.1 weight percent water in it. Model 5a had a final maximum pressure of 1.03 bar composed of 0.8 bar of N$_2$ and 0.23 bar of H$_2$. The chemistry is different in these models because there is more O$_2$ available in model 4. The chemistry of containers not linearly scaled in both volume and mass are different.

Model	V_g	V_g (cm^3)	Initial atm.	SA (m^2/g)	P$_{max}$ (bar)
4	Eq. 2	52.5	Air	5	1.1
5	Eq. 2	4.5	Air	5	6.38
5a	Eq. 2	4.5	Air	5	1.03

Table 5: Models 4 and 5. The effect of non-linear scaling.

Our fifth point is the effect of temperature. If water is present above a few monolayers and the temperature is high enough – the pressure of the storage container is due to most of the water being in the vapor phase. The pressure appears to decrease over time. The slow kinetics are due to the differences in radiolysis rates of liquid and vapor water.

Our sixth point is the effect of initial atmosphere. Since H_2 production can not take place until all of the O_2 has been consumed, pressurization will happen sooner in an inert atmosphere as compared to air. To extend the time before pressurization occurs to any extent, the cans should be filled with oxygen. Also, since the hydrogen does not grow to appreciable levels until the oxygen has been consumed, there is no possibility, according to this model, of a flammable mixture being generated inside the storage container.

Conclusion:

This model reproduces experimental pressures[5] to within a factor of 1.5 and predicts the trends for hydrogen very well. The model that uses eq 2 to calculate the head space is probably more representative of experiments than the model that used the $V_g = V_t \cdot 0.4$ approximation.

The surface area is a major contributor to the pressurization of the can. Understanding the effect of calcination on the specific surface area of the material is critical to predicting the gas composition and pressure during long-term storage. It appears that the larger the surface area the more water the system can tolerate, because ~0.22 mg/m^2 of water is tied up in the formation of the first monolayer.[9,2,1] In order to use modeling to predict the long-term gas composition and pressure, the temperature should be monitored carefully.

The results of this modeling are much more accurate if we compute the head space via equation 2. The resulting pressure rises faster than linear with the amount of water inside the can. If the volume of the can and the reagents are scaled linearly than the pressure is the same regardless of the size of the system. If the reagents and the volume of the can are scaled non-linearly the pressure inside the can after 1500 days of storage calculated using Lyman 35, is different than the pressure present in the linearly scaled 3013-99 storage containers. If water is present above a few monolayers and the temperature is high enough – the pressure of the storage container is due to all of the water, except the water in the monolayer, in the vapor phase. Since H_2 production can not take place until all of the O_2 has been consumed, pressurization will happen sooner in an inert atmosphere as compared to air.

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