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PRESSURIZATION OF CONTAINMENT VESSELS FROM PLUTONIUM OXIDE CONTENTS

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ABSTRACT

Transportation and storage of plutonium oxide is typically done using a convenience container to hold the oxide powder which is then placed inside a containment vessel. Intermediate containers which act as uncredited confinement barriers may also be used. The containment vessel is subject to an internal pressure due to several sources including; (1) plutonium oxide provides a heat source which raises the temperature of the gas space, (2) helium generation due to alpha decay of the plutonium, (3) hydrogen generation due to radiolysis of the water which has been adsorbed onto the plutonium oxide, and (4) degradation of plastic bags which may be used to bag out the convenience can from a glove box. The contributions of these sources are evaluated in a reasonably conservative manner.

NOMENCLATURE

E	average specific energy for alpha particle, W·y/mol
$e^-_{H_2O}$	number of electrons in absorbed water
e^-_{mat}	number of electrons in oxide mixture
G_{app}	apparent G value based on total oxide mass, mol/y/W
m_{H_2O}	mass of absorbed water, g
m_{PuO_2}	mass of plutonium oxide, g
m_{salt}	mass of salt in oxide mixture, g
n_{nyl}	number of moles of nylon monomer in plastic bag
P_a	ambient pressure, psia
P_{He}	helium partial pressure, psi
P_{heat}	pressure increase due to heating, psi
P_{rad}	partial pressure due to alpha radiolysis of absorbed water, psi
P_{therm}	partial pressure due to thermolysis of nylon bag, psi
P_{tot}	total pressure during storage, psi
q_0	specific radiolytic heating rate for PuO_2, W/g
Q_0	radiolytic heating rate, W
Q_{H_2O}	rate of energy deposition in absorbed water, W
R	gas constant, 1.206 psia L/mol/K
r_{nyl}	number of moles of water vapor per mole of nylon monomer generated by thermolysis
t	storage time, y
T_a	ambient temperature, K
T_1	gas storage temperature, K
V_1	gas volume, L
$\rho_{g,1}$	gas density at storage temperature and one atmosphere pressure, mol/L

INTRODUCTION

For transportation of nuclear materials, pressurization of containment vessels is a required determination per 10 CFR 71.

The Maximum Normal Operating Pressure (MNOP) is determined during Normal Conditions of Transport (NCT) including solar insolation. The containment vessel internal pressure is computed by accounting for all pressurization sources. The MNOP is then used to evaluate the containment vessel design per the ASME BPVC. Similar evaluations are required for plutonium oxide storage.[1]

CALCULATION OF TOTAL GAS GENERATION RATE FOR STORAGE OF ACTINIDE MATERIALS

The pressurization of containment vessels used to store actinide materials is due to heating of the gas inside the vessel and the generation of additional gas by alpha particle decay, radiolysis of adsorbed moisture, and thermolysis of plastics. The total pressurization of the gas inside the inner containment vessel is calculated as the sum of these contributions:

$$P_{tot} = P_{rad} + P_{therm} + P_{heat} + P_{He} \tag{1}$$

The pressure increase due to heating of the gas is calculated by applying the ideal gas law. This gives

$$P_{heat} = P_a \left(\frac{T_1}{T_a} - 1 \right) \tag{2}$$

Calculations of pressure increases due to alpha particle decay, radiolysis of absorbed water, and thermolysis of plastics are described in the following sections.

MODELING OF RADIOLYTIC GAS GENERATION RATES

The pressurization due to the generation of gas by radioactive decay is calculated by assuming that each radioactive decay by alpha emission creates one atom of helium which enters the gas space. The half-lives of those isotopes which decay by alpha emission are much longer than the time required for transport. Due to the relatively long half-lives, only a negligible fraction of the radioactive isotopes decay, and the mass of the isotopes remains essentially unchanged. Therefore, the rate of helium generation may be considered to be constant over the transport time. The rate of helium generation is proportional to the decay power divided by the energy per decay. The partial pressure of helium inside a containment vessel at any given time is (adapted from [1])

$$P_{He} = \frac{Q_0 t}{E} \frac{RT_1}{V_1} \tag{3}$$

The energy per decay for the alpha emitters that are typically shipped varies over a small range. Using the decay energy for ^{239}Pu, the pressure equation is

$$P_{He} = 7.517 \text{x} 10^{-5} \left(\frac{Q_0 t T_1}{V_1} \right) \tag{4}$$

Hydrogen and other gases also are generated by radiolysis, primarily due to alpha particle ionization of absorbed water molecules. The generation of these gases by radiolysis is commonly correlated using the G value, which is expressed in molecules of gas generated per 100 eV of deposited radioactive decay energy. If the G value is weighted by a deposition factor that is equal to the fraction of electrons present in water molecules, then it scales approximately as the G value for the alpha radiolysis of water. The G value for the generation of hydrogen by water radiolysis is 1.6 molecules/100 eV.[2] Fig. 1 compares measured hydrogen G values for plutonium oxides loaded with moisture and various salts [3,4,5] with the G value for water. It may be seen that the average G values for the oxide mixtures are roughly equivalent to the G value for water except at low moisture levels. The drop in the G value at moisture for moisture levels below about 0.5 wt% is attributed to the formation of a physisorbed or chemisorbed water layer on the oxide surface (water that is not chemically bound, however it is difficult to remove).

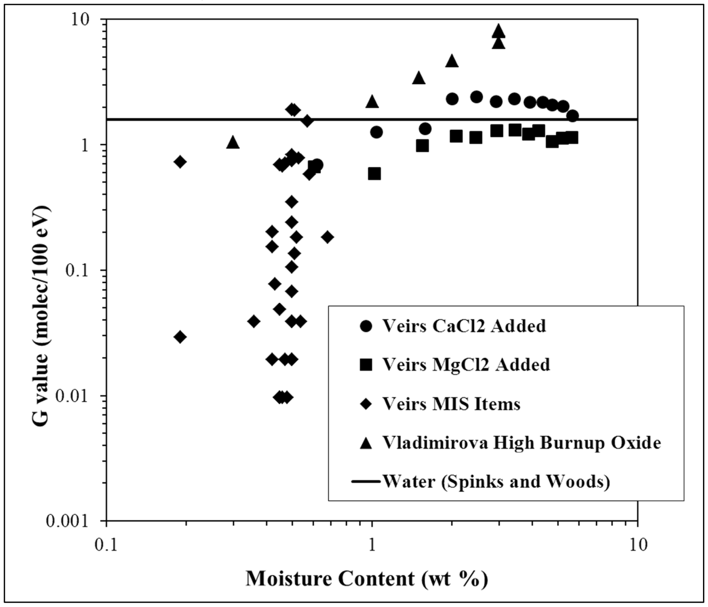

FIG. 1 VARIATION OF G VALUES FOR HYDROGEN GENERATION WITH WATER CONTENT AND COMPARISON WITH G VALUE FOR ALPHA RADIOLYSIS OF WATER

In this analysis, it is assumed that the plutonium oxide absorbs any oxygen generated by radiolysis and that the oxide material is packaged under an inert atmosphere. Under these conditions, the only gas generated by water radiolysis is hydrogen.

To estimate the radiolytic gas generation rate for 3013 packaged oxides, Kelly et al. [3] recommend the use of characteristic G values that depend primarily on the impurity content of the oxide. The basis for assigning the characteristic G values is MIS (Material Identification and Surveillance) Small Scale Surveilance pressurization data. The recommended G values are 1.1 molecules/100 eV for plutonium oxide containing a significant chloride concentration, 0.4 molecules/100 eV for oxide containing no chloride but a significant magnesium concentration, and 0.15 molecules/100 eV for fairly pure oxide.

These G values are based on the decay energy deposited in the adsorbed water. The fraction of the decay energy deposited in the adsorbed water is equal to the fraction of the electrons in the material that are associated with the water.

$$\frac{Q_{H_2O}}{Q_0} = \frac{e^-_{H_20}}{e^-_{mat}} \tag{5}$$

where

$$e^-_{H_2O} = m_{H_2O}\left(\frac{10}{18}\right) \tag{6}$$

and

$$e^-_{mat} = m_{PuO_2}\left(\frac{110}{271}\right) + m_{salt}\left(\frac{1}{2}\right) + m_{H_2O}\left(\frac{10}{18}\right) \tag{7}$$

The numerical coefficients in Eq. 7 are the number of electrons in the compound divided by the compounds formula weight. Eq. 7 uses plutonium dioxide as an example; a similar formula can be derived easily for other nuclear materials.

To compute the pressure increase due to radiolysis, it is convenient to express the G value as a function of the total oxide weight in units of mol/y/W, using Eqs. 5 through 7. The apparent G values for chloride-containing oxide, magnesium-containing oxide, and pure oxide, for an assumed moisture level of 0.5 wt%, are 0.0075, 0.0027, and 0.0010 molecules/100 eV, or 0.0246, 0.0089, and 0.0034 mol/y/W.

In terms of the apparent G value, the pressure increase due to radiolysis is

$$P_{rad} = \frac{14.696 G_{app} Q_0 t}{\rho_{g,1} V_1} \tag{8}$$

where, for storage of PuO_2, Q_0 is given by the product of the mass of oxide and the specific radiolytic heating rate, q_0:

$$Q_0 = m_{PuO_2} q_0 \tag{9}$$

The specific heating rate for typical oxides stored in 3013/9975 containers range from 0.00253 w/g Pu (0.0023 W/g PuO_2) for freshly processed weapons grade Pu to 0.00448 W/g Pu (0.00395 W/g PuO_2) for aged fuel grade Pu.[1] The specific heating rate increases slightly with time due to ingrowth of ^{241}Am by beta decay of ^{241}Pu.

Plastics and other organic materials also generate hydrogen and other gases through radiolysis. For polyethylene and PVC, the g-values for hydrogen formation are as high as 4 and 0.7, respectively.[6] The G-values for gas generation are higher, especially for PVC where much of the gas generated is HCl. Reasonable G-values for total gas generation are 4.1 for polyethylene and 8.8 for PVC.[6] These value can decrease with time due to matrix depletion. For the purposes of this calculation, the plastic is considered to be shielded by the convenience can and does not undergo radiolysis.

MEASUREMENT AND MODELING OF GAS GENERATION RATES FOR PLASTIC PACKAGING

It is assumed that the plutonium oxide is packaged in nylon bags weighing a total of 50 g. The Rocky Flats Environmental Test Site (RFETS) and the Savannah River Site (SRS) historically used nylon bags for packaging; the RFETS bags were nylon 6-6 and the SRS bags were nylon 6. Typically, the plutonium oxide is enclosed within a convenience can that shields the plastic bags from any significant radioactive dose, so there is no radiolysis of the plastic. However, the convenience can does not provide a gas seal, so any gas present either inside or outside the convenience can is subject to pressurization due to vaporization of water absorbed by the plastic (the process of thermolysis).

The thermolysis of organic materials occurs rapidly compared to radiolysis, so, for intermediate and long term storage, only equilibrium gas pressures are required. Equilibrium thermolysis pressures have been measured for nylon 6 and nylon 6-6 bagging materials. Table 1 lists the measured equilibrium pressures.

TABLE 1 EQUILIBRIUM PRESSURE INCREASES FOR OUTGASSING OF NYLON BAGGING MATERIALS

Temperature (°F)	Nylon 6-6 21 g/L	Nylon 6 21 g/L	Nylon 6-6 28 g/L	Nylon 6 28 g/L
	Press. (psig)	Press. (psig)	Press. (psig)	Press. (psig)
225	9.5	8.9	12.7	11.9
250	12.5	11.7	16.7	15.6
350	17.0	24.1	22.7	32.1
400	19.8	26.3	26.4	35.1
450	21.3	25.1	28.4	33.5
550	27.8	32.5	37.1	43.3

A comparison of the measurements at 21 and 28 g nylon/L container capacity shows that the equilibrium pressure increases are strictly proportional to the amount of nylon in the container. Therefore, the amount of outgassing is not limited by the vapor pressure of the volatile gases but instead is solely a function of temperature. It makes sense, then, at least for moderate loadings of organics as in this case, to express the equilibrium thermolysis pressure increase in terms of the number of moles of gas generated per mole of nylon monomer. A monomer unit is, for this calculation, defined as containing the average molecular weight per mole of carboxyl/amine group, which for both nylon 6 and nylon 6-6 is 113.16 g/mol. Fig. 1 shows the variation of the equilibrium gas generation with temperature up to the melting point (255 °C or 491 °F for nylon 6-6 and 220 °C or 428 °F for nylon 6), as shown by Fig. 2.

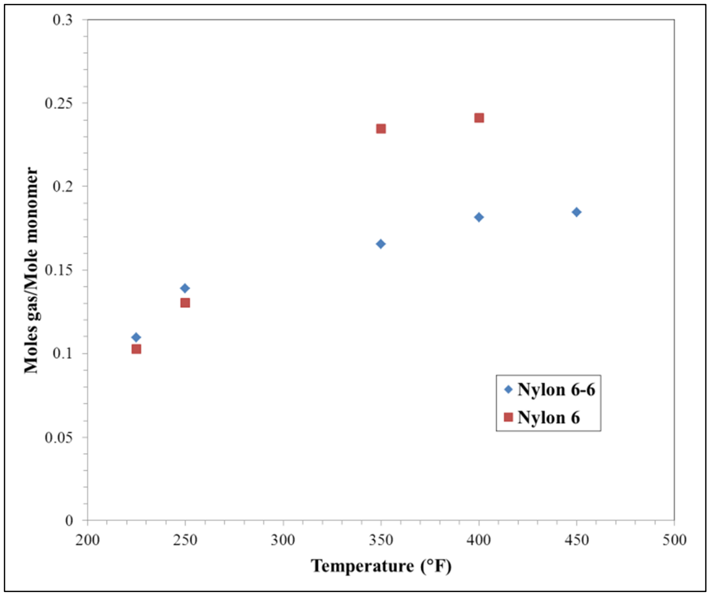

FIG. 2 OUTGASSING OF NYLON 6 AND NYLON 6-6 AS FUNCTIONS OF TEMPERATURE

To obtain the test results in Fig. 2, freshly unpackaged nylon samples were conditioned by exposure to 75% relative humidity air for 24 hours prior to heating. The weight gains during this exposure were 5.0 % for nylon 6-6 and 4.6 % for nylon 6, which corresponds to 0.31 and 0.28 moles water/mole monomer. Vaporization of this water would account for all of the pressure changes measured during the tests, plus some excess. This comparison demonstrates the sensitivity of the outgassing pressure to the degree of hydration of the nylon at the start of storage and to the packaging methods.

For storage of plutonium oxides, the thermolysis temperature depends on the degree of insulation provided by the packaging, the density of the oxide, the radiolytic decay heat rate, and the ambient temperature. Gupta [7] calculated a maximum gas temperature of 305 °F in the innermost convenience container and 285 °F in the second innermost container of a 3013 enclosure in a 9975 shipping package, based on steady state finite element heat transfer analyses for various can contents. This analysis assumes that the thermal insulation provided by the 3013 enclosure is bounding for any packaging and therefore assigns a storage temperature of 300 °F for the plastic.

It is assumed that the ambient temperature at the time of packaging is 77 °F (25 °C) and that the relative humidity is at its high bounding level of 75%. These two assumptions allow a direct prediction of the number of moles of water vapor generated by thermolysis from the measured results listed in Table 1 and shown by Fig. 2. Linear interpolation of these results gives equilibrium thermolysis ratios of 0.152 and 0.182 mol H_2O/mol monomer for nylon 6 and nylon 6-6, respectively. This analysis uses the average of these two ratios, 0.167 mol H_2O/mol monomer, to estimate the rate of water vapor generation by thermolysis. In terms of this average ratio, the rate of water vapor generation by thermolysis is given by

$$P_{therm} = \frac{n_{nyl} r_{nyl} P_a}{\rho_{g,1} V_1} \qquad (10)$$

RESULTS AND DISCUSSION

Pressure histories are calculated for PuO_2 mixtures in 9975 package. Inside the 9975 containment vessel, the PuO_2 is stored in a convenience can within an inner containment vessel. The convenience can has a slip lid which does not provide a pressure seal; the inner containment vessel is sealed. The free volume available for storage of the oxide powder inside the convenience can is assumed to be 1.839 L.[8] The total gas space within the inner containment vessel, include the convenience can interior, is 2.068 L.[8] It is assumed that 0.050 L of this volume is occupied by nylon storage bags, at a weight of 50 g and a density of approximately 1.0 g/cm^3. In the pressure history calculation, the bulk density of the oxide powder is treated as a variable to obtain the remaining free volume, under the assumption that the bulk powder fills the convenience can. The gas displacement volume for the powder is based on the crystalline density of PuO_2, which is 11.46 g/cm^3.[9]

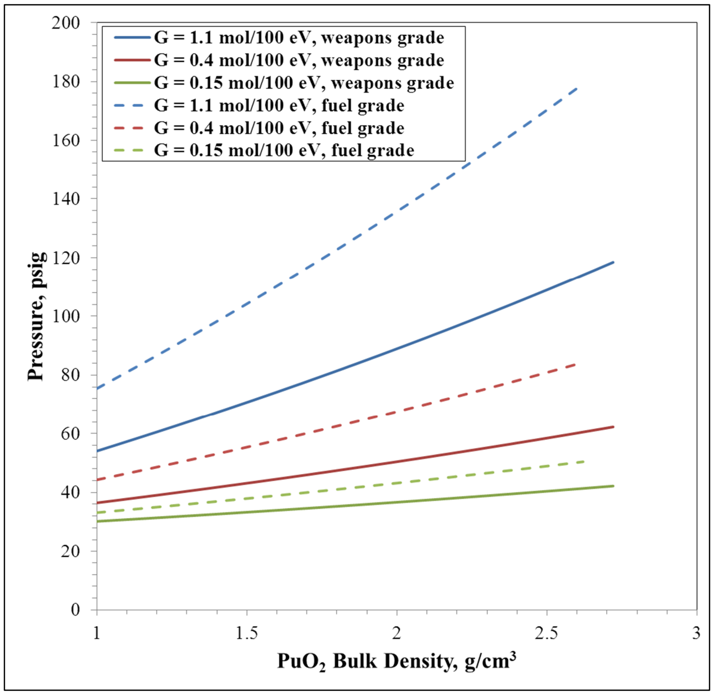

FIG. 3 VARIATION OF 9975 INNER CONTAINMENT VESSEL PRESSURES AFTER ONE YEAR STORAGE

Figs. 3 and 4 compare results for pressure history calculations for oxides containing freshly processed weapons grade Pu and aged fuel grade Pu for the range of G values specified in the previous section. Fig. 3 plots the inner containment vessel pressure after one year of storage. The pressures range from 30.2 psig to 179 psig depending on the G value, the Pu isotopic composition, and the oxide bulk density. The bulk density range for the weapons grade oxide is limited by the maximum total mass of 5 kg, and the bulk density range for the fuel grade oxide is limited by the maximum heating rate of 19 w. Approximately 26 psig to 32 psig of the total pressure increase can be attributed to direct heating, either due to volumetric expansion of the gas initial present in the vessel or due to thermolysis of the nylon bag material.

Fig. 4 depicts the variation of the storage time required to reach an inner containment vessel pressure of 100 psig, over the same bulk density ranges. These storage times range from 0.47 y to 19.1 y.

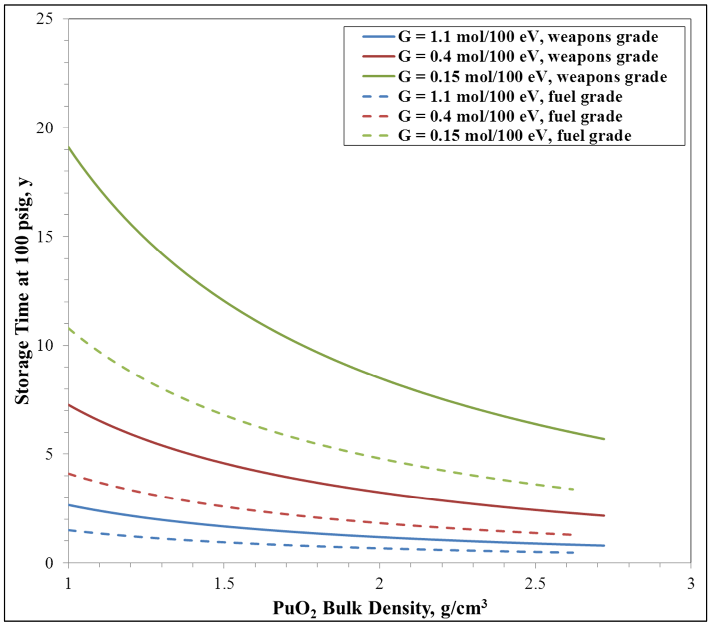

FIG. 4 STORAGE TIME REQUIRED TO REACH 100 PSIG IN 9975 INNER CONTAINMENT VESSEL

It should be noted that although these evaluations are an attempt to compute realistically conservative pressures inside containment vessels, there is opportunity for improvement. For example, the temperature used in all calculations is constant, and is based on the Normal Conditions of Transport with insolation. Nevertheless, the evaluation provides insight into the effects of plutonium oxide density, plastic bagging material, and more realistic approach to hydrogen generation via radiolysis of adsorbed moisture. Pressures in general are well below 100 psig inside the primary containment vessel other than when the most conservative G-values are used.

CONCLUSION

A realistically conservative evaluation of containment vessel pressures for plutonium oxide contents is presented. The packaging configuration is assumed to be a bagged out convenience container within a 9975 package. The sources of pressurization of containment vessels are well known, however the contribution from radiolysis and degradation of plastic bagging material is often very conservatively applied whereas the other sources can be more accurately determined. For typical amounts of stored oxide, G values for water radiolysis, and Pu isotopic composition, the total pressure in a 9975 inner containment vessel can range from 32.2 psig to 179 psig after one year. Times to reach a vessel pressure of 100 psig can vary from 0.47 y to 19.1 y depending on plutonium density, isotopic specification and G-value assumed for radiolysis. In general, pressures are below 100 psig.

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