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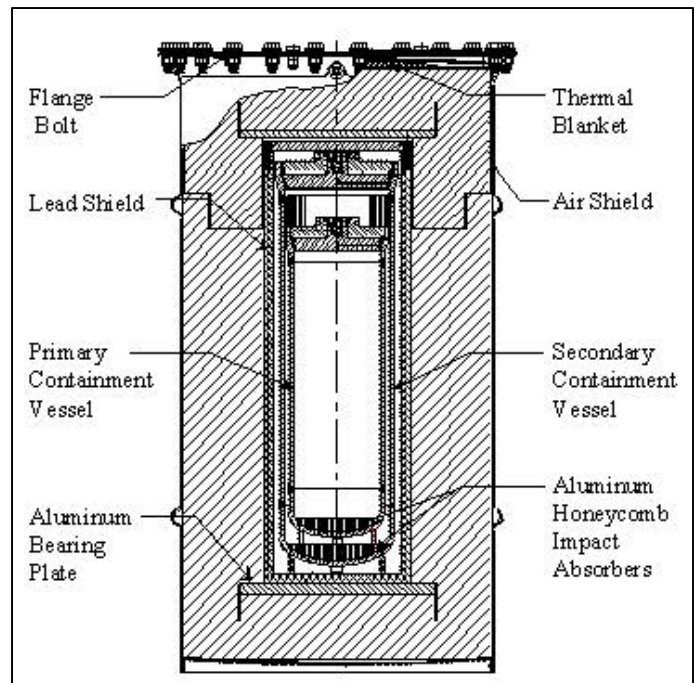
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FLAMMABILITY ANALYSIS FOR ACTINIDE OXIDES PACKAGED IN 9975 SHIPPING CONTAINERS**James E. Laurinat**Savannah River National Laboratory
Savannah River Site, Aiken, SC 29808
Email: james.laurinat@srnl.doe.gov**Neal M. Askew**Savannah River National Laboratory
Savannah River Site, Aiken, SC 29808
Email: neal.askew@srnl.doe.gov**Steve J. Hensel**Savannah River National Laboratory
Savannah River Site, Aiken, SC 29808
Email: steve.hensel@srnl.doe.gov**ABSTRACT**

Packaging options are evaluated for compliance with safety requirements for shipment of mixed actinide oxides packaged in a 9975 Primary Containment Vessel (PCV). Radiolytic gas generation rates, PCV internal gas pressures, and shipping windows (times to reach unacceptable gas compositions or pressures after closure of the PCV) are calculated for shipment of a 9975 PCV containing a plastic bottle filled with plutonium and uranium oxides with a selected isotopic composition. G-values for radiolytic hydrogen generation from adsorbed moisture are estimated from the results of gas generation tests for plutonium oxide and uranium oxide doped with curium-244. The radiolytic generation of hydrogen from the plastic bottle is calculated using a geometric model for alpha particle deposition in the bottle wall. The temperature of the PCV during shipment is estimated from the results of finite element heat transfer analyses.

INTRODUCTION

Radiolytic gas generation rates, PCV internal gas pressure, and shipping windows are calculated for the shipment of a 9975 PCV containing a plastic container of mixed actinide oxide with a selected isotopic composition. Fig. 1 shows a cross-sectional view of the 9975 shipping drum. The PCV is the innermost container shown in Fig. 1; the plastic container with the actinide oxide would be placed inside the PCV.

**FIG. 1 CROSS-SECTIONAL VIEW OF 9975 SHIPPING DRUM**

Several packaging cases are analyzed using different levels of mixed actinide oxide adsorbed moisture and different PCV gas space purge conditions. In some cases, the PCV gas space

is purged with an inert gas to drop the oxygen level below the Limiting Oxygen Concentration (LOC), in order to prevent a flammable gas mixture due to PCV internal hydrogen generation. In the absence of an inert gas purge step of the PCV, it is generally accepted that the shipping window should be limited to prevent the accumulation of hydrogen gas in excess of its Lower Flammability Limit (LFL), which is 4 vol % [1]. Accordingly, the analysis evaluates shipping windows to reach the hydrogen LFL. The analysis also computes the maximum pressure generated due to radiolysis of plastic packaging materials and all adsorbed moisture, assuming all other safety-related packaging restrictions are observed.

The radiolytic gas generation rate calculations use a plutonium isotopic composition obtained for Canada Deuterium Uranium (CANDU) reactor fuel, which is assumed to be representative of the isotopic composition of a typical mixed actinide oxide that is packaged in a 9975 PCV. The mixed actinide oxide material is modeled using the isotopic composition and moisture content for a mixed oxide prepared by adding uranium oxide to reprocessed CANDU fuel. The nominal composition for this oxide is 20 wt % PuO₂ and 80 wt % U₃O₈.

NOMENCLATURE

A	Antoine equation parameter	G _{pe}	G-value for flammable gas generation from alpha decay for polyethylene, 4.1 molecules/100 eV
A _{surf}	surface area of the bottom and sides of the bottle, cm ²	G _{PuO₂}	intrinsic G-value for hydrogen generation from plutonium oxide, molecules/100 eV
B	Antoine equation parameter	G _{U₃O₈}	intrinsic G-value for hydrogen generation from uranium oxide, molecules/100 eV
C	Antoine equation parameter	H	separation distance between alpha particle and plastic surface, cm
\dot{E}_{Pu}	plutonium specific decay energy, MeV/min/g	L ²	weighting factor for alpha particle deposition
$\dot{E}_{Pu,Pu}$	plutonium specific decay energy for plutonium oxide test, MeV/min/g	M	alpha particle atomic mass, g/mole
E _α	alpha particle energy, MeV	m _{Pu}	mass of plutonium, g
f _{dep}	fraction of alpha particle energy deposited in the polyethylene bottle wall	m _{PuO₂}	mass of plutonium oxide, g
f _O	weight fraction oxygen in the mixed oxide	m _{Pu,Pu}	mass of plutonium for the plutonium oxide test, g
f _{Pu}	weight fraction plutonium in the mixed oxide	m _{ox,s}	mass of oxide within one alpha particle range of the bottle surface, g
f _U	weight fraction uranium in the mixed oxide	m _{ox,tot}	total mass of oxide in the bottle, g
G	intrinsic G-value for hydrogen generation based on the mass of adsorbed water, molecules/100 eV	m _U	oxide mass for the uranium oxide test, 0.00586 kg
G _{app}	apparent G-value for hydrogen generation based on the total mass, molecules/100 eV	m _{U₃O₈}	mass of uranium oxide, g
G _{app,Pu}	apparent G-value for radiolytic hydrogen generation for plutonium oxide test, based on the total oxide mass, molecules/100 eV	N _A	Avogadro's number, 6.022E23 molecules/mol
G _{app,U}	apparent G-value for radiolytic hydrogen generation for uranium oxide test, based on the total oxide mass, molecules/100 eV	n _{H₂}	hydrogen content in the PCV, mol
G _b	effective G-value for the bottle wall, molecules/100 eV	n _{Pu}	total number of plutonium atoms in the absorber
		n _U	total number of uranium atoms in the absorber
		n _O	total number of oxygen atoms in the absorber
		$\Delta \left(\frac{dn_{H_2}}{dt} \right)_{Pu}$	change in rate of radiolytic hydrogen generation for the plutonium oxide test per change in adsorbed moisture fraction, 15.5 nmol/hr on a 1.0 g oxide basis
		$\left(\frac{dn_{H_2}}{dt} \right)_{max}$	maximum rate of hydrogen generation to keep below the LFL, mol/hr
		P _{max}	maximum pressure inside the PCV, psig
		P _{max,ref}	reference maximum pressure due to radiolytic hydrogen generation, from the hydrogen back pressure tests, psig
		P _a	ambient pressure, 14.696 psia
		P _{v,H₂O}	saturation vapor pressure of water at the gas temperature inside the PCV, psia
		$\left(\frac{dP}{d\alpha_d} \right)_U$	rate of pressure increase as a function of alpha dose for the uranium oxide test, torr/MGy
		R	distance between an alpha particle and the plastic surface, cm
		R _g	ideal gas law constant, 82.057 cm ³ atm/mol/K
		R _{tot}	range of alpha particles in the mixed oxide, mg/cm ²

R_Z	alpha particle range in element Z, mg/cm ²
R_a	alpha particle range in air, mg/cm ²
R_{Pu}	range of alpha particles in plutonium, mg/cm ²
R_O	range of alpha particles in oxygen, mg/cm ²
R_U	range of alpha particles in uranium, mg/cm ²
T_{ref}	temperature for the Duffey and Livingston tests, assumed to be 293.15 K
T	temperature inside the PCV, K
$T_{a,tr}$	reference ambient temperature for transportation of the 9975 cask, 370.15 K
T_{ref}	reference average gas temperature in PCV for transportation of the 9975 cask, 429.15 K
T_r	reference temperature, 273.15 K
t_{LFL}	time to reach the LFL for hydrogen, days
Δt_{max}	shipping window, days
V_{LFL}	volume of hydrogen at the LFL at the reference pressure (the initial pressure in the PCV prior to radiolytic gas generation), cm ³
V_{H_2}	volume of hydrogen gas, cm ³
y_{LFL}	volume fraction hydrogen at the LFL, 0.04 [1]
V_U	gas volume for the uranium oxide test, 11.61 cm ³
V_g	gas space volume inside the PCV, cm ³
W_{Pu}	rate of alpha energy deposition, W
$W_{Pu,ref}$	reference rate of alpha energy deposition for the 9975 container, 19 W
x_{H_2O}	mass fraction adsorbed moisture
$x_{H_2O,b}$	mass fraction of adsorbed water bound to the surface and not participating in radiolysis
$x_{H_2O,U}$	mass fraction adsorbed moisture for uranium oxide test, 0.10
$\Delta x_{H_2O,Pu}$	change in adsorbed moisture mass fraction for the plutonium oxide test, 0.008
Z	atomic number of element Z
θ	angle at which an alpha particle strikes the plastic surface ($\theta = 0$ is perpendicular), radians
$\rho_{M,g}$	molar density of gas in the PCV, mol/cm ³
$\rho_{M,g,U}$	molar gas density for the uranium oxide test, mol/cm ³
ϕ	angle, radians
ω	angle, radians

VARIABLES FOR PARAMETRIC ANALYSIS

Several hypothetical cases are examined to determine the effects of oxide mass and moisture content, with and without purging of the PCV gas space with inert gas prior to shipment. The various cases considered include one calculation of the shipping window to prevent the accumulation of a flammable gas mixture and four calculations of the maximum pressure that can develop due to radiolytic gas generation and heating. Two cases take credit for the existence of an upper pressure limit for radiolytic gas generation due to the effect of hydrogen back pressure and three do not credit this back pressure effect.

Experiments conducted by Duffey and Livingston [2] indicate that the maximum pressure that can be developed inside the PCV is limited by hydrogen back pressure within the PCV. Their experiments showed that a hydrogen back pressure of 25 psig was sufficient to prevent radiolytic hydrogen generation from fuel grade plutonium oxide calcined at 700 °C, and that a back pressure of 82 psig was required to prevent hydrogen generation from weapons grade plutonium oxide calcined at 450 °C. The fuel grade oxide composition is considered to be representative of the mixed actinide oxide, while the 82 psig back pressure for the weapons grade oxide is deemed to be a worst case bounding maximum pressure for oxides calcined at low to moderate temperatures. The 82 psig back pressure would increase to 123 psig if it is assumed that radiolysis of the adsorbed moisture generates both hydrogen and oxygen in a stoichiometric ratio of one part oxygen for every two parts hydrogen and that the partial pressure of hydrogen is the controlling back pressure.

The other parameter that is varied for the maximum pressure calculations is the stoichiometry of the radiolysis reaction. For the calculation of the maximum pressure due to radiolytic heating and gas generation, it is assumed that there is concurrent generation of one mole of oxygen for every two moles of hydrogen from water radiolysis. To be conservative, generation of oxygen is not included in the calculation of the shipping window for Cases 1, 2, and 3. (Omission of the oxygen generation from the shipping window calculation is conservative in that the additional oxygen dilutes the hydrogen concentration by half of the relative amount of hydrogen that is formed. The reduction at the LFL is 2 % of 4 vol %, or 0.08 vol %.) For Cases 4 and 5, hydrogen back pressure limits are calculated for radiolytic hydrogen generation with and without concurrent oxygen generation. The back pressure limits represent the maximum pressures that would result solely from radiolysis, without considering flammability limits. Table 1 summarizes the conditions used for each of the cases analyzed.

TABLE 1
PARAMETRIC CASES FOR 9975 PCV SHIPPING ANALYSIS

Case No.	Oxide (kg)	H ₂ O (wt %)	Gas Purge	Back Press. (psig)	O ₂ Gen.	Shipping Window
1	1.2	2.5	No	None	Yes	Calculated
2	1.2	2.5	No	None	Yes	90 ^a
3	5.0	2.5	No	None	Yes	90 ^a
4	5.0	^b	Yes	82	No	365+
5	5.0	^b	Yes	123	Yes	365+

^a The shipping window is assumed to be 90 days. The hydrogen generation rate that would give a 90-day shipping window is calculated.

^b The hydrogen back pressure limit is independent of the moisture level.

ANALYSIS OVERVIEW

The rate of hydrogen generation due to alpha radiolysis of moisture adsorbed on the oxide is calculated using the G-value, which is defined as the number of molecules of gas generated per 100 eV of alpha particle energy absorbed. The G-values are fit to measurements of hydrogen generation rates obtained for fuel grade plutonium oxide (Duffey and Livingston [2]) and for uranium oxide spiked with curium-244, a short half-life alpha emitter (Icenhour and Toth [3]). The calculated G-values are adjusted for the moisture content of the mixed oxide.

The rate of flammable gas generation due to alpha radiolysis of the polyethylene or polyvinyl chloride (PVC) bottle is computed using an analysis of alpha energy deposition from oxide that is within one alpha particle range of the bottle surface. It is assumed that the oxide coats the bottom and side walls of the bottle. The G-value for that portion of the alpha energy that is deposited in the plastic is 4.1 molecules/100 eV; this G-value is applicable for either polyethylene or PVC [4]. It is assumed that this G-value is applicable for generation of flammable gases by interaction of the mixed actinide oxide with the surrounding plastic container. The flammable gases are primarily hydrogen and thus are treated as hydrogen in the flammability calculations.

The G-value is multiplied by the plutonium content of the packaged material and the specific power of the plutonium in MeV/min/g Pu to obtain the rate of radiolytic gas generation. Compared to that of plutonium, the activity of the uranium in the mixed actinide oxide is sufficiently low to be considered insignificant. Isotopic compositions for the CANDU mixed oxide and the fuel grade oxide used by Duffey and Livingston were used to compute the specific powers for these oxides. The specific power of the CANDU oxide is 9.31E-03 W/g Pu (2.20E12 MeV/min/g Pu), and the specific power of the fuel grade oxide is 3.22E-03 W/g Pu (1.20E12 MeV/min/g Pu). The specific power is calculated from the isotopic Pu composition of the materials, summarized in Table 2.

PCV internal pressure also can increase due to heating of gases inside the PCV, and due to outgassing of water vapor by the plastic bagging material and container. The maximum temperature is estimated from a thermal analysis for solar heating during transportation of a 9975 cask [5]. This analysis determined that the average gas temperature inside a PCV was 156 °C for transportation of plutonium oxide with a heat generation rate of 19 W, and a 9975 external ambient temperature of 37.8 °C. The calculation of the PCV gas temperature includes the effect of insolation.

TABLE 2
ISOTOPIC COMPOSITION AND SPECIFIC POWER FOR CANDU AND SRS FUEL GRADE PLUTONIUM OXIDES

CANDU Oxide			SRS Fuel Grade Oxide		
Isotope	Mass Fraction	Specific Power (W/g Pu)	Isotope	Mass Fraction	Specific Power (W/g Pu)
Pu-238	0.0018	1.00E-03	Pu-238	0.00096	5.35E-04
Pu-239	0.6567	1.24E-03	Pu-239	0.838	1.59E-03
Pu-240	0.2787	1.94E-03	Pu-240	0.153	1.07E-03
Pu-241	0.0	0.0	Pu-241	0.0081	2.85E-05
Pu-242	0.0204	2.33E-06	Pu-242	0.0002	2.28E-08
Am-241	0.0459	<u>5.12E-03</u>	Am-241	0.0	<u>0.0</u>
Total		9.31E-03	Total		3.22E-03

This temperature is scaled to the heat generation rate for the amount of actinide oxide stored in the PCV. The calculation of the maximum PCV pressure does not account for the small rate of pressure increase due to helium gas generation. The pressure change due to potential outgassing is limited to the saturation vapor pressure of water at the gas temperature inside the PCV.

The calculation of the time required to reach the LFL for hydrogen requires use of the gas space volume inside the PCV. The gas space volume is calculated by subtracting the volumes occupied by the oxide, the bottle plastic, the lead liner, and any other plastic bagging from the interior volume of the PCV. The PCV volume is 5128 cm³, minus 45 cm³ for an aluminum honeycomb spacer, for an empty volume of 5083 cm³. The plastic container volume is calculated by dividing the mass of an empty 1-L bottle, measured to be 95 g, by the density of polyethylene, 1.35 g/cm³, to get 70 cm³. It is assumed that there are 100 g of plastic bagging material, which, at a nylon density of 1.084 g/cm³, occupies 92 cm³. The volume occupied by the lead bottle liner is not known and is neglected in calculating the total gas volume. The volume of the mixed actinide oxide is based on the particle density, calculated as 90% of the theoretical or pycnometric density of the mixed oxide [6]. The theoretical density of the mixed oxide is calculated from the densities of plutonium oxide, 11.46 g/cm³, and of uranium oxide, 8.30 g/cm³ [7], and the density of water, 1.0 g/cm³, for the adsorbed moisture.

The dimensions of the bottle are needed to compute the inside surface area exposed to alpha radiolysis from the mixed oxide. The height of a 1-L polyethylene bottle was measured to be 200 mm, and the outer diameter was measured to be 94 mm.

The time to reach the LFL for hydrogen generation is computed by dividing the volume of hydrogen gas inside the PCV at the LFL by the rate of radiolytic hydrogen generation:

$$t_{LFL} = \frac{V_{LFL}}{\left(\frac{dV_{H_2}}{dt}\right)} \quad (1)$$

The volume of hydrogen gas at the LFL equals the product of the total gas volume inside the PCV and the ratio of the volume of hydrogen gas to inert gas at the LFL:

$$V_{LFL} = \frac{y_{LFL}}{1 - y_{LFL}} V_g \quad (2)$$

The hydrogen volume at the LFL is referenced to the pressure inside the PCV prior to any radiolytic gas generation. The volume fraction hydrogen in the denominator accounts for the compression of the gas as radiolytic hydrogen is formed.

The volumetric rate of radiolytic hydrogen generation equals the molar rate of hydrogen generation divided by the molar volume of gas in the PCV:

$$\frac{dV_{H_2}}{dt} = \frac{1}{\rho_{M,g}} \frac{dn_{H_2}}{dt} \quad (3)$$

The molar gas density is calculated from the ideal gas law.

Hydrogen is generated by radiolysis of both the adsorbed moisture in the oxide and the polyethylene in the bottle wall. The molar rate of radiolytic hydrogen generation is given by the following expression.

$$\frac{dn_{H_2}}{dt} = \frac{(10000)(60)(24)(G_{app} + G_b)\dot{E}_{Pu} m_{Pu}}{N_A} \quad (4)$$

G-VALUE CALCULATION FOR THE OXIDE

The apparent G-value is computed as a function of an intrinsic G-value based on the mass of adsorbed moisture, by applying a rule that the fraction of the alpha energy absorbed by the moisture is proportional to the fraction of electrons present in the adsorbed water [8]. This rule gives the relation

$$G_{app} = G \left(\frac{(x_{H_2O} - x_{H_2O,b}) \left(\frac{10}{18}\right)}{x_{H_2O} \left(\frac{10}{18}\right) + (1 - x_{H_2O}) \left(\frac{m_{PuO_2} \left(\frac{110}{271}\right) + m_{U_3O_8} \left(\frac{340}{842}\right)}{m_{PuO_2} + m_{U_3O_8}} \right)} \right) \quad (5)$$

The mass fraction of adsorbed water bound to the surface is set at 0.005 (0.5 wt %), based on the results of the Duffey and Livingston tests [2].

The overall intrinsic G-value is computed as a weighted average of individual G-values for the plutonium oxide and uranium oxide present in the mixed oxide, with a weighting factor equal to the number of electrons in each oxide constituent. This gives

$$G = \frac{m_{PuO_2} G_{PuO_2} \left(\frac{110}{271}\right) + m_{U_3O_8} G_{U_3O_8} \left(\frac{340}{842}\right)}{m_{PuO_2} \left(\frac{110}{271}\right) + m_{U_3O_8} \left(\frac{340}{842}\right)} \quad (6)$$

As stated previously, the intrinsic G-values for uranium oxide are evaluated based on tests using curium-244 doped with uranium oxide, performed by Icenhour and Toth [3], and the intrinsic G-value for plutonium oxide is evaluated based on tests performed using SRS fuel grade plutonium oxide, performed by Duffey and Livingston [2]. The uranium oxide G-value is calculated from the results from Sample A-2-2 from the Icenhour and Toth report. This sample was spiked with 10 wt % water. The G-value is calculated directly from the initial rate of pressure increase per unit alpha dose. The initial rate of pressure increase, from Fig. 2, was 146.58 torr/MGy.

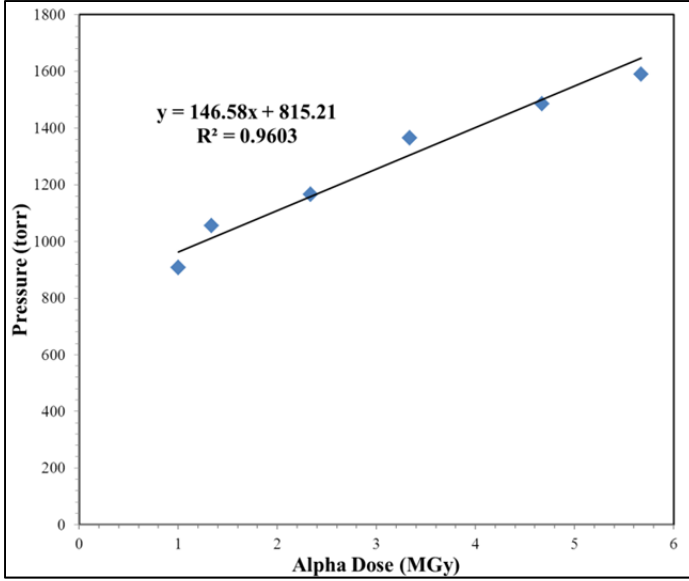


FIG. 2 REGRESSION OF INITIAL RATE OF PRESSURE INCREASE FOR ICENHOUR AND TOTH TEST

The following equation is used to convert this rate to an apparent G-value:

$$G_{app,U} = \frac{(1.609E-19)(100)N_A}{(760)(1.0E6)} \frac{\rho_{M,g,U} V_U}{m_U} \left(\frac{dP}{d\alpha_d} \right)_U \quad (7)$$

The molar gas density for this expression is calculated from the ideal gas law, based on a pressure of 1.0 atm and the temperature at which the test was conducted, 27 °C.

The G-value for plutonium oxide is set to match the measured hydrogen generation rate in air over fuel grade plutonium oxide measured by Duffey and Livingston for fuel grade plutonium oxide calcined at 700 °C, which was 19.375 nmol/g/h/wt % moisture for moisture levels above 0.5 wt %. The measure rate in nmol/hr/g is related to the apparent G-value based on the total mass of oxide by

$$\frac{\Delta \left(\frac{dn_{H_2}}{dt} \right)_{Pu}}{\Delta x_{H_2O,Pu}} = \frac{(1.0E13)(60)G_{app,Pu} \dot{E}_{Pu,Pu} m_{Pu,Pu}}{N_A} \quad (8)$$

The intrinsic G-values for uranium oxide and plutonium oxide, calculated from Eqs. (5) and (6), are 1.68 and 1.19 molecules/100 eV, respectively. The weighted average for a mixed oxide containing 20 wt% plutonium oxide and 80 wt % uranium oxide is 1.29 molecules/100 eV. This G-value is only slightly lower than the G-value for radiolysis of liquid water, which has been reported to be 1.6 molecules/100 eV [9].

The G-value for radiolytic flammable gas generation for the polyethylene bottle walls is calculated by multiplying the G-value for polyethylene by the fraction of the oxide that is within one alpha particle range of the wall and by the fraction

of the alpha decay energy that deposits from all oxide that is within one particle range. It is assumed the oxide covers the bottom and side surfaces of the bottle. The effective G-value for the bottle wall is given by

$$G_b = G_{pe} f_{dep} \left(\frac{m_{ox,s}}{m_{ox,tot}} \right) \quad (9)$$

The analysis conservatively assumes that the oxide coats the bottle walls at its theoretical density. The gas spaces within the microsphere material are ignored, since the particle range through gas dwarfs the range in the solid oxide. Therefore, the mass of oxide that is assumed to be within one particle range of the bottle wall is the product of the particle range in mg/cm² and the surface area covered by the particles, which is assumed to be the sum of the interior bottom and side surfaces:

$$m_{ox,s} = \frac{A_{surf} R_{tot}}{1000} \quad (10)$$

ANALYSIS OF DEPOSITED ENERGY FOR ALPHA PARTICLES IN PLASTIC

Alpha particles lose significant fractions of their energies within the mixed oxide, so that the absorbed dose decreases with increasing distance from the polyethylene bottle surface. The rate of energy transfer from alpha particles to the mixed oxide is correlated in terms of particle ranges, defined as the particle travel distance, or stopping distance, divided by the absorber material density. The general correlation for the alpha particle range in the mixed oxide composed of element Z is [10]

$$\frac{R_Z}{R_a} = 0.90 + 0.0275Z + (0.06 - 0.0086Z) \log \left(\frac{E_\alpha}{M} \right) \quad (11)$$

Special cases of this correlation apply for low atomic weight materials. These are, for $Z < 10$,

$$\frac{R_Z}{R_a} = 1.0 + (0.06 - 0.0086Z) \log \left(\frac{E_\alpha}{M} \right) \quad (12)$$

and for hydrogen,

$$\frac{R_Z}{R_a} = 0.30 + (0.06 - 0.0086Z) \log \left(\frac{E_\alpha}{M} \right) \quad (13)$$

The alpha particle range in air is correlated by the following power law fit to a chart of range in air versus alpha energy [10]. The fit was obtained by plotting data from the chart as shown by Fig. 3.

$$R_a = 0.2952E_\alpha^{1.6283} \quad (14)$$

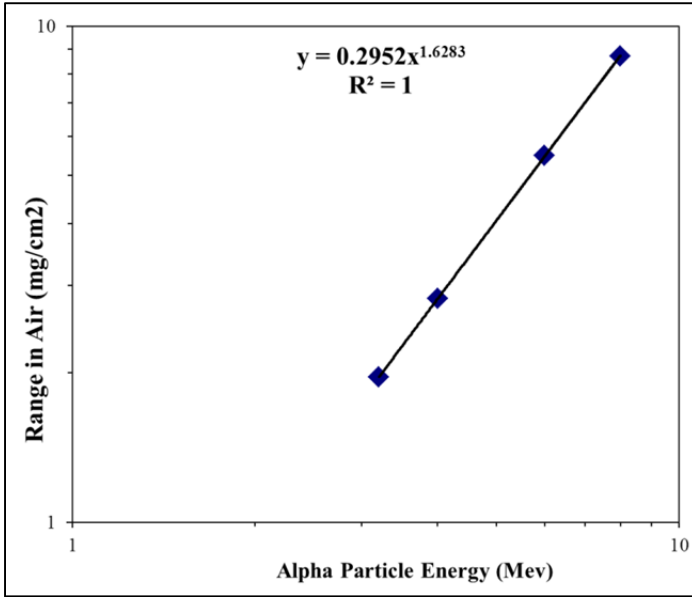


FIG. 3 CORRELATION OF ALPHA PARTICLE RANGE IN AIR

The mixed oxide constitutes a composite material comprised of plutonium, uranium, and oxygen. The alpha particle range in this composite material is given by the reciprocal sum [10]

$$R_{\text{tot}} = \frac{1}{\frac{f_{\text{Pu}}}{R_{\text{Pu}}} + \frac{f_{\text{U}}}{R_{\text{U}}} + \frac{f_{\text{O}}}{R_{\text{O}}}} \quad (15)$$

The following section presents a derivation of the fraction of the alpha decay energy which deposits in the bottle wall. The fractional energy deposition is computed from the observation that an alpha particle must be within one particle range of the bottle surface for any deposition to occur. It may be recalled that the alpha particle range defines the maximum travel distance of an alpha particle in the mixed oxide. If it is assumed that an alpha particle deposits its energy at a uniform rate along its range, then the deposited energy, i.e., the alpha dose, is deposited at a rate inversely proportional to the square of the distance from particle source out to a radius equal to the particle range.

The geometry for the particle deposition is illustrated by Fig. 4. Let L^2 be the weighting factor for the alpha particle energy deposition rate at a distance $H = R \cos(\theta)$ between the fissile atom and the surface. L^2 varies inversely as the square of the distance from the fissile isotope. Let θ be the angle at which the alpha particle strikes the surface. (When $\theta = 0$, the particle strikes the surface at a perpendicular angle.)

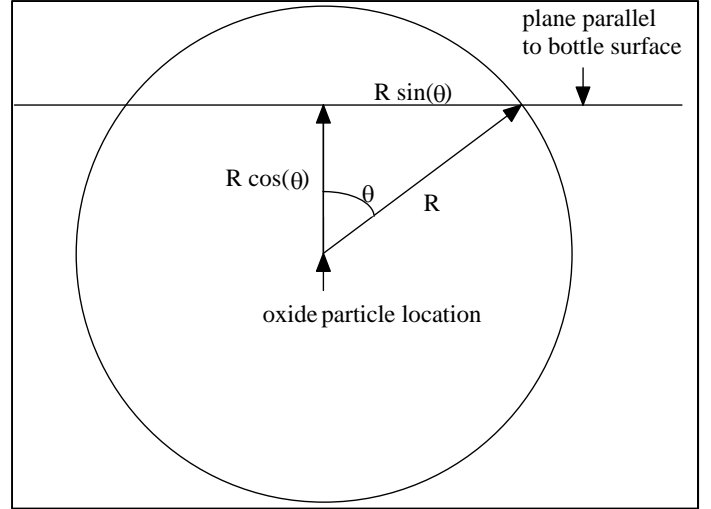


FIG. 4 SCHEMATIC REPRESENTATION OF ALPHA PARTICLE RANGE IN RELATION TO THE LINER SURFACE

The average weighting factor $\langle L^2 \rangle$ for a separation distance H is the area integral for the circular cross-section where the surface subtends the spherical volume bounding the travel of the alpha particles. Thus,

$$\frac{1}{L^2} = \frac{1}{R^2 (\cos^2(\theta) + \sin^2(\phi))} \quad (16)$$

and

$$\frac{1}{\langle L^2 \rangle} = \frac{\int_0^{\sin(\theta)} \frac{R^2 \sin(\phi) d\sin(\phi)}{L^2}}{\int_0^{\sin(\theta)} R^2 \sin(\phi) d\sin(\phi)} = -\frac{2 \ln(\cos(\theta))}{R^2 \sin^2(\theta)} \quad (17)$$

The overall weighting factor for the separation distance H is the volume integral of this term:

$$\int_{\cos(\theta)}^1 \frac{1}{\langle L^2(\phi) \rangle} \pi R^3 \sin^2(\phi) d\cos(\phi) = \pi R (2 - 2 \cos(\theta) + 2 \cos(\theta) \ln(\cos(\theta))) \quad (18)$$

At the maximum separation distance $H = R$ this volume integral is:

$$\int_0^1 \frac{1}{\langle L^2(\phi) \rangle} \pi R^3 \sin^2(\phi) d\cos(\phi) = 2\pi R \quad (19)$$

The average weighting factor for the separation distance range $0 \leq H \leq R \cos(\omega)$ is:

$$\int_0^{\cos(\omega)} \int_{\cos(\theta)}^1 \frac{1}{\langle L^2(\phi) \rangle} \pi R^3 \sin^2(\phi) d\cos(\phi) d\cos(\theta) = \pi R \left(2\cos(\omega) - \frac{3}{2}\cos^2(\omega) + \cos^2(\omega) \ln(\cos(\omega)) \right) \quad (20)$$

Thus, the average weighting factor for the total range $0 \leq H \leq R$ is:

$$\int_0^1 \int_{\cos(\theta)}^1 \frac{1}{\langle L^2(\theta) \rangle} \pi R^3 \sin^2(\phi) d\cos(\phi) d\cos(\theta) = \frac{1}{2} \pi R \quad (21)$$

The multiplier is this average weighting factor divided by twice the weighting at the maximum separation distance. (The factor two appears because alpha particles travelling away from the surface do not reach the surface.) The multiplier is given by:

$$f_{\text{dep}} = \frac{\int_0^1 \int_{\cos(\theta)}^1 \frac{1}{\langle L^2(\phi) \rangle} \pi R^3 \sin^2(\phi) d\cos(\phi) d\cos(\theta)}{2 \int_0^1 \int_{\cos(\theta)}^1 \frac{1}{\langle L^2(\phi) \rangle} \pi R^3 \sin^2(\phi) d\cos(\phi) d\cos(\theta)} = \frac{1}{8} \quad (22)$$

CALCULATION OF PRESSURE INCREASE FROM RADIOLYSIS

As stated previously, there is a maximum pressure that can be attained due to radiolytic hydrogen generation, as indicated by hydrogen back pressure tests conducted by Duffey and Livingston [2]. It is assumed that this maximum pressure increases due to heating of the gas inside the PCV from radiolytic heat generation. The expression for the total pressure increase, including heating effects and pressure increases due to outgassing of water vapor from the plastic bagging material and the polyethylene bottle, takes the form

$$P_{\text{max}} = (P_{\text{max,ref}} + P_a) \left(\frac{T}{T_{\text{ref}}} \right) - P_a + P_{\text{v,H}_2\text{O}} \quad (23)$$

As stated previously, a gas temperature of 156 °C was calculated for normal transportation of plutonium oxide in a 9975 cask, based on a radiolytic thermal power of 19 W [5]. Both the thermal power and the gas temperature are significantly higher than for transportation of the mixed oxide. The gas temperature for the mixed oxide is scaled on the results for the 19 W material using a linear interpolation, as recommended by the DOE 3013 Standard [6]. The reference temperature for zero heat generation, which accounts for

insolation, is 97 °C [6]. The temperature of the gas inside the PCV for transportation of the mixed oxide is estimated from the following interpolation formula.

$$T = \left(\frac{W_{\text{Pu}}}{W_{\text{Pu,ref}}} \right) (T_{\text{ref}} - T_{\text{a,tr}}) + T_{\text{a,tr}} \quad (24)$$

The heating rate for the mixed oxide in this expression is calculated from the specific decay energy and mass of the mixed oxide, using the equation

$$W_{\text{Pu}} = \frac{(1.609\text{E}-13) \dot{E}_{\text{Pu}} m_{\text{Pu}}}{60} \quad (25)$$

The water vapor pressure is given by the following Antoine formula [11]:

$$P_{\text{v,H}_2\text{O}} = \left(\frac{14.696}{760} \right) 10^{\left(A - \left(\frac{B}{T - T_r + C} \right) \right)} \quad (26)$$

where

$$A = 8.07131, \quad B = 1730.63, \quad \text{and} \quad C = 233.426 \quad (27)$$

when $T < 373.15 \text{ K}$.

DISCUSSION OF RESULTS

The objective of this calculation is to determine the allowable shipping window (time after loading a PCV that will result in compliance with 9975 safety basis) during which the hydrogen concentration inside the PCV will not exceed the LFL. Three quantities related to the shipping are calculated, the maximum rate of radiolytic hydrogen generation for a 90-day shipping window, the shipping window for the analyzed mixed actinide oxide material, and the maximum pressure inside the PCV for the analyzed oxide material. The first quantity is the maximum rate of radiolytic hydrogen generation for which the hydrogen concentration remains below the LFL for a 90-day period. This is given by

$$\left(\frac{dn_{\text{H}_2}}{dt} \right)_{\text{max}} = \frac{1}{24\Delta t_{\text{max}}} \left(\frac{y_{\text{LFL}}}{1 - y_{\text{LFL}}} \right) \left(\frac{V_g P_a}{R_g T} \right) \quad (28)$$

The maximum molar gas generation rate to allow for a 90-day shipping window, calculated using Eq. (28), is 3.74E-06 mol/hr.

Table 3 summarizes the results for the cases listed in Table 2. For Case 1, the estimated molar gas generation is 2.77E-05 mol/hr, the shipping window for the hydrogen concentration to remain below the LFL for Case 1 is 12.1 days, and the pressure at the end of the shipping window is 20.8 psig. The increase in the pressure includes contributions from

heating of the gas initially present in the PCV, evaporation of adsorbed moisture, and radiolytic generation of stoichiometric amounts of hydrogen and oxygen from the adsorbed moisture and plastic material in the PCV. The amount of radiolysis, the temperature, and hence the pressure remain the same for Case 2. For Case 3, the pressure at the end of the shipping window is 36.4 psig; the increase from the pressures for Cases 1 and 2 is due to an increase in the gas temperature and water vapor pressure for the increased oxide loading.

TABLE 3
RESULTS FOR PARAMETRIC CASES FOR 9975 PCV
SHIPPING ANALYSIS

Case No.	Oxide (kg)	H ₂ O (wt %)	Gas Purge	O ₂ Gen.	Ship Window (days)	Press. (psig)	H ₂ Gen. Rate (mol/hr)
1	1.2	2.5	No	Yes	12.1	20.8	2.77E-05
2	1.2	2.5	No	Yes	90	20.8	3.74E-06
3	5.0	2.5	No	Yes	90	36.4	3.74E-06
4	5.0	^a	Yes	No	365+	118.7	----
5	5.0	^a	Yes	Yes	365+	159.7	----

^a The hydrogen back pressure limit is independent of the moisture level.

Cases 4 and 5 give the maximum pressures for storage of plutonium oxide in a 9975 PCV, without regard to hydrogen flammability limits. The maximum pressures are 118.7 psig if only hydrogen is generated by water radiolysis and 159.7 psig if there is concurrent generation of a stoichiometric amount of oxygen. These pressures are based on the Duffey and Livingston hydrogen back pressure measurements for radiolysis of moisture adsorbed on weapons grade plutonium oxide calcined at 450 °C. The increases from the back pressures listed in Table 2 (82 and 123 psig) are primarily due to evaporation of adsorbed moisture, which adds 31.5 psig. The remainder of the difference is caused by heating of the gases initially present in the PCV.

Most of the radiolytic hydrogen generation is from moisture adsorbed onto the surfaces of the mixed oxide. For Cases 1 and 2, approximately 7.6% of the hydrogen generation is from the plastic in the PCV. The fraction of radiolysis from plastic is lower for the remaining cases.

CONCLUSIONS

The methodology for calculating allowable windows for transporting actinide oxides in plastic bottles inside 9975 shipping containers is described. The shipping window is limited to prevent the accumulation of a flammable gas mixture in the PCV gas space due to radiolysis of moisture adsorbed on the oxide and of the plastic container. It is shown that the flammability criterion can be satisfied by limiting either the duration of the shipping window or the mass and moisture

content of the oxide. The calculation of the rate of radiolytic hydrogen generation from adsorbed moisture is benchmarked with results from gas generation tests using plutonium oxide and doped uranium oxide. A geometric model is developed to predict the rate of alpha particle deposition in the plastic and the rate of flammable gas generation due to plastic radiolysis. The flammability calculations show that the maximum molar gas generation rate to allow for a 90-day shipping window is 3.74E-06 mol/hr. At the estimated molar gas generation for 1.2 kg of mixed oxide of 2.77E-05 mol/hr, the shipping window for the hydrogen concentration to remain below the LFL is 12.1 days.

If the PCV is filled with inert gas prior to shipment, then the gas mixture inside the PCV will not become flammable. For shipments with an inert gas purge, the rate of pressure increase is calculated. The pressure increases as a result of radiolytic gas generation, evaporation of moisture from both the oxide and the plastic bottle and bagging material, and radiolytic heating of the compressible gases inside the PCV. The maximum pressure inside the PCV due to radiolytic hydrogen generation is estimated to be 118.7 psig, based on hydrogen back pressure tests for weapons grade plutonium oxide calcined at 450 °C. This pressure would rise to 159.7 psig if there is concurrent generation of a stoichiometric quantity of oxygen.

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