Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

SRNS-STI-2016-00056

DRAFT

Proceedings of the ASME 2016 Pressure Vessels & Piping Division Conference
PVP2016
July 17-21, 2016, Vancouver, BC, Canada

PVP2016-63024

EVALUATION OF POLYVINYL CHLORIDE BAGS DURING PLUTONIUM STORAGE

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ABSTRACT

This evaluation considers the storage of plutonium materials in 9975 shipping packages at the Savannah River Site (SRS) K-Area Complex (KAC). The materials are packaged in a can – bag – can configuration where the outer can is a screw lid filtered can and the inner can is a slip lid filtered can (filters for both cans are located in the can lid). The inner slip lid can is secured using polyvinyl chloride tape. A filtered plasticized polyvinyl chloride (pPVC) bag is used to bag out the slip lid can from the glove box where the plutonium oxide is packaged. The filtered bag and slip lid can are placed into the outer screw lid can outside the glove box. This can – bag – can configuration is packaged into a 9975 shipping package for storage. An empty "dummy" tin plated carbon steel can (with a hole in the lid) is packaged on top of the screw lid can inside the 9975 Primary Containment Vessel (PCV). The threshold heat generation such that the thermal decomposition of the pPVC bag is precluded is 7 Watts. In addition, the maximum 9975 PCV pressure is computed for normal conditions of storage of the 9975 shipping package in K-Area Complex (KAC).

INTRODUCTION

Some of the plutonium oxide materials stored at SRS are stabilized per DOE-STD-3013 [1], however, not all containers are welded 3013 containers. Rather, they are packaged into a stainless steel filtered slip lid convenience container (approximately 870 cc) with the lid secured using polyvinyl chloride tape and bagged out of the processing glove box using either a filtered pPVC bag or a filtered polyethylene bag. Per the 9975 Safety Analysis Report for Packaging (SARP), the maximum mass of plastic allowed for a SARP-compliant shipping package is 100 grams. The bagged can is next packaged into a screw lid stainless steel container. This can – bag – can configuration is packaged into a 9975 shipping package for storage at the SRS KAC. An empty "dummy" tin plated carbon steel can (with a hole in the lid) is packaged on top of the screw lid can inside the 9975 PCV.

Polyvinyl Chloride

Polyvinyl chloride (PVC) is the third-most commercially produced thermoplastic and it has many excellent properties. PVC is commonly used in either rigid form (e.g. pipe) or in a flexible (plasticized) form, denoted as pPVC. However, as with all polymers, PVC can degrade due to several mechanisms including thermal degradation (thermo-oxidation in air), ionizing-radiation damage, and ultraviolet (UV) light degradation (photo-oxidation). A degradation mechanism specific to PVC and certain other chlorine-containing polymers is dehydrochlorination, which primarily results in HCl gas generation. In this application, UV degradation is not a concern.

Radiolytic Effects on Plasticized Polyvinyl Chloride Bags

Radiation interacts with the pPVC plastic bag via incident gamma radiation from the plutonium inside the inner container and via alpha particle radiation from plutonium oxide contamination on the inner surface of the bag. For pPVC bag material, the primary products of these radiolytic interactions are HCl and hydrogen gas generation.

For a conservative evaluation of radiolysis of pPVC, the total gas generation G-value is assumed to be comparable to that for polyethylene. G-values for pure PVC films and powders are considerably higher but are not believed to be applicable for end-use products. For additional conservatism, a factor of 2 increase in the G-value of polyethylene results in 6.8 molecules/100 eV which for a highly contaminated bag results in a total of 0.52 cc of hydrogen at standard temperature and pressure per year. Given the free volume of the 9975 PCV is greater than 3,000 cc, the effect of gas generation due to radiolysis of a pPVC bag and tape is considered negligible. Thus, the radiolysis of the pPVC bag results in negligible gas generation for up to 10 years of storage.

Thermal Degradation of Polyvinyl Chloride

Concerns regarding the thermal decomposition of pPVC contamination bags were identified in an Assessment of Plutonium Storage Safety conducted by the Department of Energy (DOE) in 1994 [2], which recommends an operating temperature limit of 85 °C to ensure the pPVC bag does not thermally decompose. Thermal decomposition results in bag failure, which may result in a contamination hazard, and generation of hydrogen chloride (HCl) gas. This gas is likely to react with steel packaging components. In addition gas generation due to thermal decomposition may also result in container pressurization. Food pack can pressurization has occurred at Savannah River Site (SRS) where pPVC bags have been utilized, although can failure did not occur [3]. Specific to packaging applications, pPVC bags have been tested at various temperatures to investigate thermal degradation [4] in the United Kingdom.

The United Kingdom testing consisted of can – bag – can configurations where an aluminum screw lid inner can was bagged using a PVC bag and placed into a sealed outer rim food pack can. The inner and outer cans were presumed to be filled with air since there is no indication that the cans were inerted (e.g. nitrogen or argon). Testing was performed at constant temperatures of 85 °C, 110 °C, and 135 °C in ovens. The testing at 110 °C and 135 °C resulted in significant bulging of the outer sealed food pack cans within weeks while the testing at 85 °C resulted in no significant changes to the package after 8 months (no indication of pressurization of the outer food pack can). According to reference 4, an operational temperature limit of 85 °C was imposed on the outer surface of the container which utilizes a pPVC bag in order to protect against thermal degradation.

These results are reasonably consistent with other reports which suggest pPVC begins to degrade in 1 – 2 months at 98°C [5] and testing performed at SRS where decomposition begins at 194°F (90°C) [6].

A conservative temperature limit of 75 °C is selected for the threshold where thermal decomposition of pPVC occurs. This conservatism accounts for variation in the glass transition temperature of the specific bag products involved and the possibility for plasticizer/stabilizer migration which would could increase HCl generation rates or lower the threshold gas generation temperature.

The principal gas products evolved due to thermal degradation and pyrolysis of PVC and its additives are HCl and benzene (C_6H_6). Thermal degradation of PVC generally proceeds in two stages: a dehydrochlorination stage in which HCl and benzene form, followed by a pyrolysis stage in which a portion of the benzene condenses to form alkyl and condensed ring aromatics, which largely deposit as tars [7]. Several references show that dehydrochlorination and HCl evolution can occur as low as 70 - 80 °C, particularly for pure, non-stabilized PVC polymer [8 - 10].

Tsuchiya and Sumi [11] tabulated the gas fraction from the pyrolysis of non-plasticized PVC powder in helium at 350 °C to be 57.9 wt. % HCl, 0.47 wt. % H_2, 3.2 wt. % CH_4, 0.32 wt. % C_2H_6, 2.5 wt. % C_2H_4, 5.9 wt. % C_6H_6, and 0.87 wt. % C_7H_8 with 37.4 wt. % condensed residue. These gases are summarized in Table 1. These data are for pyrolysis of PVC in helium (not air), which reasonably represents the pPVC bag in an inerted atmosphere with limited oxygen. These gases, and in particular, the average gas molecular weight of 32.25 g/g_{mol} provides a basis for calculating theoretical maximum storage pressures for storage conditions greater than 75 °C.

Table 1: pPVC Thermal Decomposition Gases for 60 g pPVC

Gas Species	Wt % of pPVC in product gas	Molecular Weight (g/g_{mol})	Gas Quantity (g_{mol})
HCl	57.9	36.5	0.9518
H_2	0.47	2	0.141
CH_4	3.2	16	0.1200
C_2H_6	0.32	30	0.0064
C_2H_4	2.5	28	0.0536
C_6H_6	5.9	78	0.0454
C_7H_8	0.87	92	0.0057
Totals	71.16	32.25 (avg)	1.3238

Analytical Methods and Computations

Threshold Heat Loading For pPVC Thermal Decomposition

A temperature criterion of 75 °C (167 °F) is used to determine the maximum allowable heat loading in the 9975 shipping container during storage conditions. A temperature of 75 °C ensures pPVC decomposition does not occur.

The maximum ambient temperature recorded in the storage area at SRS was approximately 32.2 °C (90 °F) during a very hot summer (approximately 10 consecutive days over 37.8 °C (100°F) during which building ventilation was malfunctioning). Typical summer maximum ambient temperatures are approximately 29.4 °C (85 °F). A conservative temperature of 36.1 °C (97 °F) is considered to be the upper bound ambient storage temperature at SRS. An additional 3.9 °C (7 °F) is added to the ambient temperature to account for localized hot spots in the storage facility (i.e. within 9975 shipping package storage arrays) based on temperature measurements within the storage area. Therefore, the effective maximum ambient temperature is 40.0 °C (104 °F).

Thermal analyses of 9975 shipping containers have been performed for nested can configurations. The maximum average PCV gas temperature during storage can be computed using the following:

$$T_{ave} = 104°\text{F} + 6\frac{°\text{F}}{Watt} * W$$

where W is heat loading in Watts and T_{ave} is average PCV gas temperature in °F. For 19 Watts, the average PCV gas temperature is 218 °F (103.3 °C).

Similarly, the outer can top temperature during storage can be computed using the following:

$$T_{can} = 104°\text{F} + 6.7\frac{°\text{F}}{Watt} * W$$

where W is heat loading in Watts and T_{can} is the outer can top temperature in °F. For 19 Watts, the outer can top temperature is 231.3 °F (110.7 °C).

The 9975 thermal analyses for nested containers also showed that for a heat loading of approximately 10 Watts, the maximum inner can temperature is 6 °C (10.8 °F) warmer than the outer can top.

In order to ensure the pPVC contamination control bag remains below 75 °C (167 °F), the heat loading must be no more than 7 Watts (shown below).

$$\frac{167°\text{F} - [104°\text{F} + 10.8°\text{F}]}{6.7\frac{°\text{F}}{Watt}} = 7.79\ Watts$$

Therefore, heat loadings of no more than 7 Watts will ensure that the pPVC contamination control bag will not thermally decompose.

Maximum Storage Pressure in 9975 Containment Vessel

The plutonium oxide materials stored using a pPVC bag and tape can be evaluated using bounding content parameters. The maximum heat loading is 19 Watts, which is the maximum heat loading permitted in the 9975 shipping package. Although the 9975 shipping package allows up to 5,000 g of plutonium oxide with up to 0.5 wt. % adsorbed moisture, the bounding parameters of this evaluation for mass of plutonium oxide is no more than 3,000 g with no more than 6 g adsorbed moisture (for 3,000 g of oxide, 6 g of adsorbed moisture equates to 0.20 wt. %). The amount of pPVC is limited to 60 grams.

Net Free Volume within 9975 PCV

The volume occupied by the plutonium oxide is presented in Table 2. The maximum volume of the slip lid convenience can is 871 cm^3. The volume occupied by the plutonium oxide is determined using the statistical density method in DOE-STD-3013 where the ratio of bulk to particle density is given by:

$$Fp = 0.3928 + 0.05673\rho_{bulk}\ ([1], p.54\ and\ p.60)$$

where ρ_{bulk} = M/871 (note that 871 cc is free volume of the slip lid can) is given in g/cm^3 and the volume occupied by the contents in cm^3 is $(M/\rho_{bulk})*F_p$, where M is the plutonium oxide mass in grams.

Table 2: Volume Occupied by Pu Oxide Contents

Parameter	Value
Convenience Can Volume	871 cm^3
Oxide Mass	3,000 g
Bulk Density of Oxide, ρ_{bulk}	3.44 g/cm^3
Packing Fraction, F_p	0.588
Volume of Oxide	512.8 cm^3
Volume of Oxide	0.0181 ft^3
Free Volume in Convenience Can	0.0127 ft^3

Metal cans used in the packaging weigh no more than 2,000 g and the metal density is 7.9 g/cm^3. Therefore, the volume of the metal cans is 2,000 g/7.9 g/cm^3 = 253.2 cm^3 or 0.00894 ft^3.

The amount of pPVC plastic (e.g. bag and tape) used during packaging is recorded by operating procedure and is restricted to be less than 60 grams. This quantity accounts for all plastics outside the inner slip lid can. The density value of 0.92 g/cm^3 bounds the density of pPVC, which is typically slightly greater than 1 g/cm^3 (note, a lower density is more conservative as it results in less free volume in the 9975 PCV). The volume of the pPVC is 60 g/0.92 g/cm^3 = 65.2 cm^3 or 0.00230 ft^3.

The gross free volume of the 9975 PCV is 0.1811 ft^3, and the volume of the honeycomb spacer is 0.0016 ft^3. These volumes have been previously determined in the 9975 SARP.

The net free volume within the 9975 PCV can be readily determined by subtracting all the components within the PCV which consume volume from the PCV gross volume. This is shown in Table 3.

Table 3: Net PCV Free Volume (60 grams pPVC)

Component	Volume (ft^3)
(1) Gross PCV Free Volume	0.1811
(2) PCV honeycomb	0.0016
(3) Cans (2000 g)	0.00894
(4) Plastic (60 g)	0.00230
(5) Pu oxide (3000 g)	0.0181
(1-2-3-4-5) Net PCV Free Volume	0.1502

<u>Number of Moles of Gas Within the PCV</u>

Sources of gas within the 9975 PCV include the initial fill gas, gas generation due to radiolysis of moisture, gas generation due to thermal decomposition of the pPVC, and helium generation due to alpha decay of the plutonium. Note that pressurization due to the evaporation of water is not included in this evaluation.

Backfill Gas

The 9975 PCV is backfilled with atmospheric pressure of 14.7 psi gas at 70 °F. The moles of fill gas in the PCV can be determined using the ideal gas law:

$$n = \frac{PV}{RT}$$

where the fill gas pressure is 14.7 psia, the net PCV free volume is 0.1502 ft^3 (Table 3), ideal gas law constant is 10.73 psi-ft^3/lb_{mol}/R, and fill gas temperature is 70 °F or 70 °F + 459.6 = 529.6 R,

$$\frac{14.7\, psia * 0.1502\, ft^3}{10.73\, \frac{psi - ft^3}{lb_{mol} - R} * 529.6\, R} = 3.885E - 4\, lb_{mol}$$

and,

$$3.885E - 4\, lb_{mol} * 453.6\, \frac{g_{mol}}{lb_{mol}} = 0.1762\, g_{mol} (\text{input to Table 4})$$

Radiolysis of Adsorbed Moisture

No more than 25% of adsorbed moisture undergoes radiolysis to generate hydrogen gas. Oxygen gas is not generated from radiolysis of adsorbed moisture; thus one mole of radiolyzed moisture results in one mole of hydrogen gas.

$$H_2O \rightarrow H_2(gas) + \frac{1}{2} O_2\ (chemically\ bounded, not\ gas)$$

Los Alamos has studied water radiolysis of stabilized plutonium oxide (per DOE-STD-3013) and concluded that no more than 25% results in hydrogen gas and oxygen gas is not generated [12]. The generation of hydrogen can be computed using 6 g of moisture and the assumption that no more than 25% of adsorbed moisture undergoes radiolysis. Using the above chemical reaction equation, the radiolysis of one mole of water generates one mole of hydrogen. The amount of moles of hydrogen produced is readily determined as:

$$6\, g\, H_2O * \frac{mol\, H_2O}{18\, g\, H_2O} * \frac{1\, mol\, H_2}{1\, mol\, H_2O} * \frac{1}{4} = 0.0833\, g_{mol}$$

Thus, the radiolysis of 6 grams of water will produce 0.0833 g_{mol} of hydrogen gas (input to Table 4).

Gas Generated by Decomposition of pPVC

The number of moles of gas generated by the thermal decomposition of 60 g of pPVC materials is determined using the data shown in Table 1. Data from Table 1 are for pyrolysis of PVC in helium (not air), which reasonably represents the pPVC bag in an inerted atmosphere with limited oxygen. Consider 60 grams of pPVC with an average molecular weight of the product gas of 32.25 g/g_{mol}. A total of 60 g of pPVC is utilized, however per Table 1 only 71.16% (or 42.7 grams), is decomposed. Thus, the amount of gas generation, in moles, due to the thermal decomposition of PVC is 42.7 g/32.25 g/g_{mol} = 1.324 g_{mol} of gas (input to Table 4).

Helium from Plutonium Alpha Decay

Helium generation from radioactive decay (i.e. alpha particle emission) of 19 Watts of plutonium occurs at a rate of 5.22E-06 lb_{mol} every 2 years [1]. All the helium is in the gas phase, which contributes to pressurization of the 9975 PCV. For 10 years of storage, this value is 2.61E-05 lb_{mol} or 0.0118 g_{mol} (input to Table 4).

Total Pressure within 9975 PCV

The total number of moles of gas within the 9975 PCV can be readily determined by summing the individual components (fill gas, radiolysis of adsorbed moisture, helium, and pPVC thermal decomposition). Note that gas generation due to radiolysis of pPVC is negligible.

Table 4: Amount of Gas in 9975 PCV

Component	Quantity (g_{mol})
(1) Fill Gas	0.1762
(2) Helium	0.0118
(3) Hydrogen	0.0833
(4) PVC Decomposition	1.3240
($\Sigma_{1\rightarrow4}$) Complete gas mixture in PCV	1.5953

The complete gas mixture in the PCV is 1.5953 g_{mol} which is 1.5953 g_{mol}*1 lb_{mol}/453.6 g_{mol} = 0.003517 lb_{mol}.

The average gas temperature within the PCV for 19 Watts of heat generation is 218 °F (103.3 °C), which is 376.45 K (677.6 R).

The total pressure in the 9975 PCV is:

$$P = \frac{nRT}{V}$$

$$P = \frac{0.003517\, lb_{mol} * 10.73\, \frac{psi - ft^3}{lb_{mol} - R} * 677.6\, R}{0.1502\, ft^3} =$$

$$P = 170.2\, psia$$

The difference between absolute pressure and gage pressure is the atmospheric pressure, which is 14.7 psig.

$$P = 170.2\, psia - 14.7\, psi = 155.5\, psig\ (1072\, kPa)$$

CONCLUSIONS

The evaluation presented in this paper considered the storage of plutonium oxides in 9975 shipping packages at SRS in KAC. The evaluation had the oxide packaged in a can – bag – can configuration. pPVC contamination control bags are also selected for this evaluation. Thermal degradation of pPVC contamination control bags is conservatively defined to occur at 75°C (167°F). This corresponds to a decay heat load of 7 Watts with a 9975 shipping package.

A shipping package configuration with a decay heat loading of 19 Watts is also evaluated. A decay heat load of 19 Watts corresponds to a pPVC contamination control bag temperature of greater than 75 °C. Thus, the 60 grams of pPVC undergoes thermal degradation and leads to the pressurization of the 9975 PCV through gas generation (e.g. hydrogen gas).

The pressurization of the 9975 PCV is dependent on the fill gas, helium generation from alpha decay, hydrogen generation through the radiolysis of adsorbed water, and gas generation through the thermal decomposition of pPVC (e.g. pPVC contamination control bag and tape). The total pressure of the 9975 PCV was determined to be 155.5 psig. Thus, based on these bounding parameters, material stored utilizing pPVC contamination control bags and tape at 19 Watts at SRS KAC is within safe handling limits.

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