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HYDROGEN FLAMMABILITY MITIGATION IN A CONTAINMENT VESSEL USING A RECOMBINER

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ABSTRACT

Plutonium oxide packaged in a 9975 Primary Containment Vessel (PCV) is evaluated in terms of preventing a flammable gas mixture due to hydrogen generation. Hydrogen is generated via radiolysis of adsorbed moisture on the plutonium oxide. A recombiner is placed in the PCV to recombine hydrogen and oxygen at concentrations to prevent hydrogen flammability. A detailed hydrogen diffusion analysis which evaluates expected and bounding conditions in order to demonstrate that hydrogen concentrations will remain below 5% by volume within PCV is presented.

INTRODUCTION

The packaging configuration consists of three inner product cans containing plutonium dioxide packaged within an outer can. Each stainless steel slip lid inner can is vented with a sintered metal filtered vent and bagged with a polyethylene filtered bag. The tin plated carbon steel slip lid outer can is also filtered with a sintered metal filter. The slip lids are secured using tape. The outer can is packaged in the 9975 PCV with the recombiner being placed on top of the outer can. The PCV has an inner diameter of 0.127 m (5 inches). Both the recombiner and outer product can are diametrically slightly smaller than the PCV. The outer can is 0.324 m (12.75 inches) tall and the recombiner is 0.057 m (2.25 inches) tall. The 9975 PCV is depicted in Figure 1.

The recombiner catalyst consists of siliconized platinum metal. Approximately 7 grams of siliconized metal are packaged in a gas permeable Tyvek bag with two bags used in the recombiner. The recombiner can is tin plated carbon steel with perforated holes. Approximately 350 grams of Type 4a zeolite molecular sieve is placed in the recombiner can to maintain a dry atmosphere within the PCV. The recombiner maintains a less than 1% hydrogen concentration at the recombiner can boundary while recombining 2.7 ml of hydrogen per minute at a hydrogen concentration below 1% in air.

The vertical spacing between the inner cans, to ensure a hydrogen diffusion pathway, is provided by an engineered spacer, such as a screen, placed between the cans. A recombiner will be placed above the outer can to ensure a flammable mixture does not occur. The recombiner prototype has been tested.

Each inner can has a sintered metal filter in the lid allowing hydrogen to diffuse out of the can. Each of the inner cans is placed in a bag with a NucFil® filter. A total of three can/bag packages are placed within the outer can. Figure 2 shows a drawing of the COMSOL™ model with a description of the domains within the model.

NOMENCLATURE

c_A	the concentration of the diffusing species (mole/cm^3),
D_{AB}	diffusivity of species A (hydrogen) through species B (air), cm^2/s
D_{eff}	effective diffusivity, cm^2/s
E	energy of alpha particle, MeV

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$\dot{E}$	total decay energy rate, MeV/s
F	fraction of alpha energy absorbed by water
G_{H_2}	G-value for hydrogen, molecules/100 eV
M	atomic mass of an alpha particle, 4 g/mole
$\dot{m}_{H_2}$	rate of hydrogen formation due to radiolysis, mole/s
M_i	atomic mass of component i, g/mole
N_A	Avogadro's number, 6.022E23 molecules/mole
R_a	alpha particle range in air, cm
R_i	alpha particle range in element i, cm
R_t	alpha particle range in the compound, cm
R_z	alpha particle range in an element with atomic number Z, cm
SP_i	relative stopping power
t	time, s
w_i	weight fraction of element i in compound
Z	atomic number
ε	porosity
τ	tortuosity

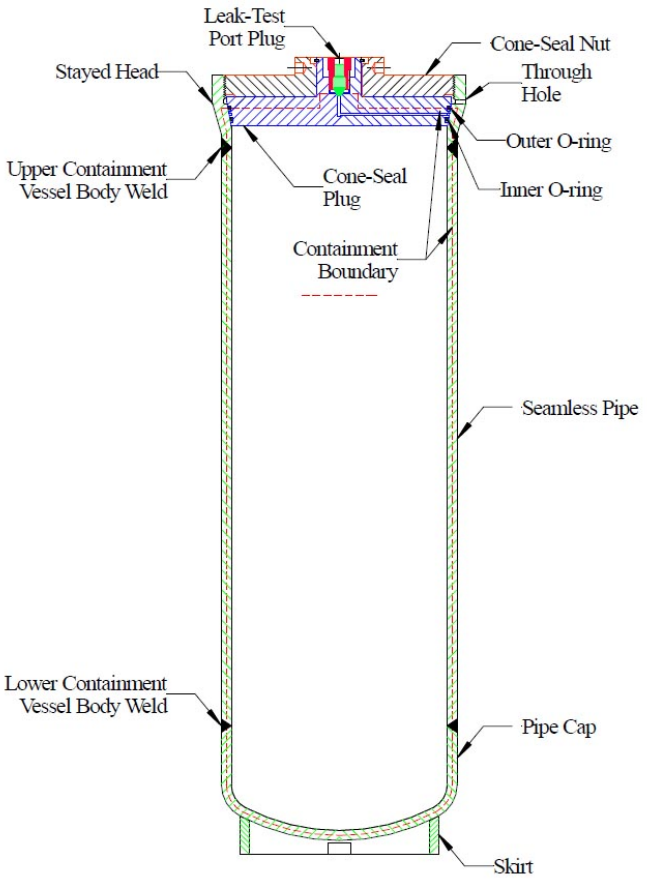

FIG 1. 9975 PRIMARY CONTAINMENT VESSEL (PCV)

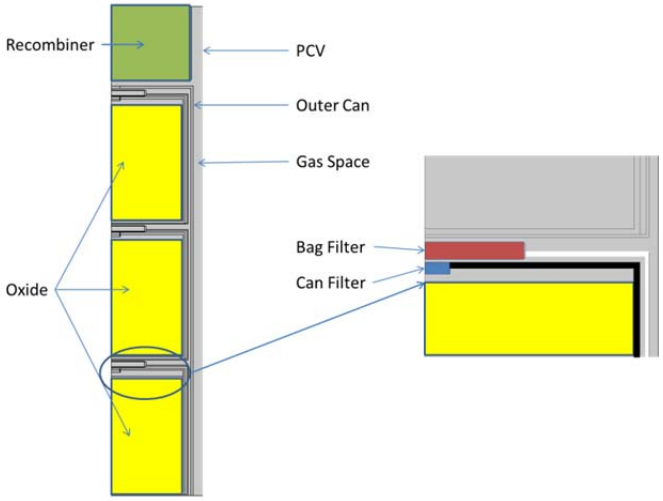

FIG 2. INNER CAN, OUTER CAN AND PCV (r-z plane)

ANALYSIS METHOD

An axisymmetric COMSOL™ Multiphysics model was created to perform hydrogen diffusion simulations. The analyses are steady-state. Hydrogen gas generation is treated as a uniform volumetric source term within the inner product cans. The rate of hydrogen generation is an input to the simulation and is based upon the moisture content of the plutonium oxide.

In general, the model mesh consists of approximately 160,600 elements. The mesh size was varied up to 400,000 with no change in the resulting steady state hydrogen concentration.

Governing Equations

The time dependent diffusion of hydrogen through air is described by the equation

$$\frac{\partial c_A}{\partial t} = D_{AB}\nabla^2 c_A \qquad (1)$$

The diffusion of the flammable species in the package is inherently two dimensional, with diffusion occurring in both the axial and radial directions. First, the hydrogen diffuses through the pores within the oxide and the void space between the oxide material represented by the porosity of the oxide. The governing equation for this diffusion is

$$\frac{\partial c_A}{\partial t} = D_{eff}\nabla^2 c_A \qquad (2)$$

The effective diffusion of the hydrogen through the oxide bed is given by equation 3.

$$D_{eff} = \frac{\varepsilon D_{AB}}{\tau} \qquad (3)$$

Next, the hydrogen must diffuse through the can filter into the outer bag region and through the NucFil® 036DA filter in the outer bag. Once outside the bag, the hydrogen diffuses around the remaining cans and through the outer can filter. Once outside of the outer can, the hydrogen diffuses through the PCV air space and is removed from the gas phase by the recombiner as long as oxygen is present. A 1.0 vol % hydrogen concentration is assigned as a boundary condition at the surface of the recombiner.

Hydrogen Gas Generation

Hydrogen generation from plutonium oxide is due to radiolysis of the adsorbed moisture. The radiolysis occurs when radiation (alpha decay) energy is adsorbed by the moisture. The fraction of the energy absorbed by water is a function of the relative stopping powers and masses of the various constituents of the materials to be shipped. The range of an alpha particle in an element can be calculated using the equation[1]

$$\frac{R_z}{R_a} = 0.90 + 0.0275Z + (0.06 - 0.0086Z)\log_{10}\left(\frac{E}{M}\right) \quad (4)$$

For elements with 2 < Z < 11 the terms 0.90 + 0.0275Z are replaced with 1.00. For hydrogen (Z = 1) the two terms are replaced by 0.30. The alpha particle energy E is set at 5.25 Mev, which is typical for plutonium isotopes.

The ranges for chemical compounds are calculated using the equation

$$\frac{1}{R_t} = \frac{w_1}{R_1} + \frac{w_2}{R_2} + \frac{w_3}{R_3} + \ldots \quad (5)$$

The relative stopping power is the reciprocal of the range R_t. The fraction of the decay energy absorbed by the water is the product of the stopping power of water and the mass of water present divided by the sum of the products of the stopping power of the materials present and their masses:

$$F = \frac{SP_{H_2O} M_{H_2O}}{\sum_i SP_i M_i} \quad (6)$$

The G-value based on total energy is then estimated by multiplying the G-value for bulk water[2] (1.6) by the fraction of energy deposited into the adsorbed water.

The hydrogen gas generation rate is calculated by

$$\dot{m}_{H_2} = \frac{10000 G_{H_2} F \dot{E}}{N_A} \quad (7)$$

The rate of hydrogen generation is a strong function of adsorbed moisture fraction. An adsorbed moisture fraction of 0.75 wt % results in a G-value of approximately 0.04 molecules/100 ev, and an adsorbed moisture fraction of 1.0 wt % results in a G-value of approximately 0.05 molecules/100 ev. For reference, 0.75 wt % results in 4.6 mL/h of hydrogen and 1.0 wt % results in 6.2 mL/h.

Additional Inputs

The hydrogen diffusion coefficient in air is 6.68E-5 m^2/s at 0 ºC. For added conservatism a value of 6.1E-5 m^2/s is used. This value is also valid for hydrogen diffusion in nitrogen. The bag filter is a NucFil® Filter with a diameter of 1 inch and a height of 0.2 inches. The filter has a hydrogen diffusion rate of 0.0001 moles/sec/mole fraction at 25 ºC. The oxide bed tortuosity is set at a value of three, based on analyses of moisture adsorption rate tests for plutonium oxide powders.[3]

DISCUSSION OF RESULTS

A number of parametric studies were performed where G-Value (adsorbed moisture), can filter porosity, can filter diameter, can filter thickness, vertical can spacing, and density of plutonium oxide were all varied. A total of 648 steady state simulations were performed. Shown in 3 is a graphic of the output. For the three oxide cans, the lowest hydrogen concentration is in the top can due to its proximity to the outer can filter. The hydrogen concentration gets progressively greater for each of the lower two cans due to the longer diffusion paths to the outer can filter.

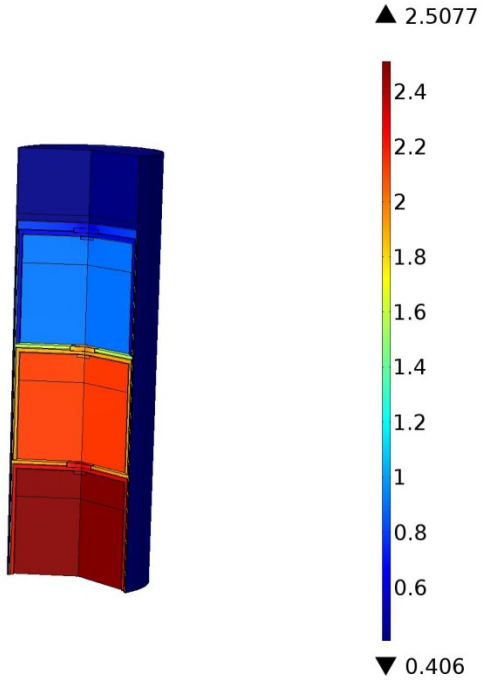

FIG 3. HYDROGEN CONCENTRATION FROM SIMULATION

A summary plot of all cases is provided in Figure 4 where maximum hydrogen concentration is plotted on the y-axis. This

plot shows that only a few cases approach a 5% vol. hydrogen concentration.

Figure 5 shows that at low hydrogen generation rates (i.e. low G values), the filter porosity does not affect the maximum hydrogen concentrations, but as the hydrogen generation rate increases, the filter begins to limit the rate of hydrogen diffusion out of the inner can. A slight trend can be seen for the maximum hydrogen concentration with respect to the inner can filter porosity.

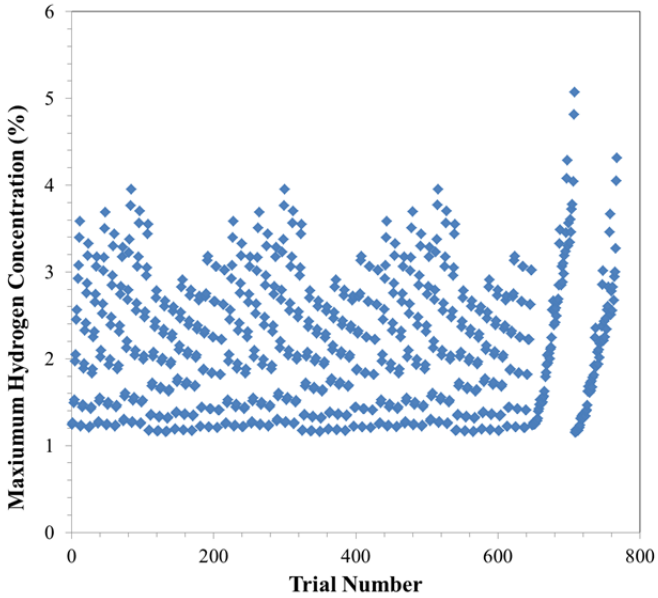

FIG 4. SUMMARY PLOT OF SIMULATIONS

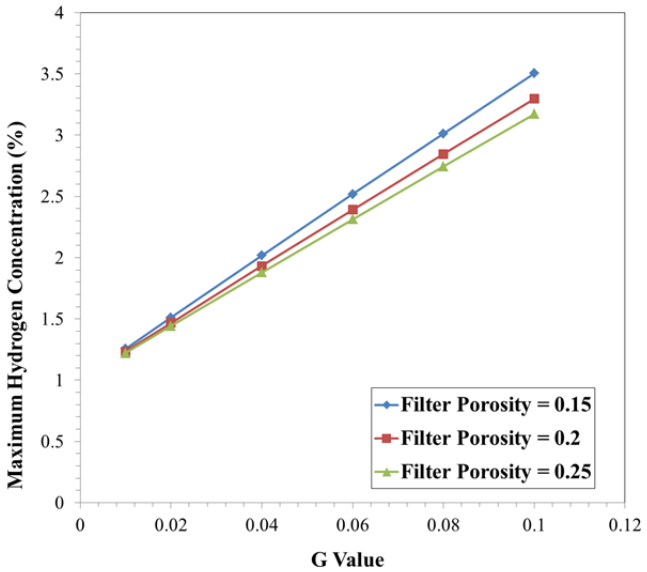

FIG 5. MAXIMUM HYDROGEN CONCENTRATION WITH FILTER POROSITY VARIATION

The canister filter diameter does have a significant influence on the maximum hydrogen concentration at steady state. Figure 6 shows two curves, one for a filter diameter of ½ inch and the other for a 1 inch diameter. Increasing the diameter, and therefore the cross sectional area available for hydrogen to diffuse out of the cans, is shown to reduce the maximum hydrogen percentage by 50% at high G-values. As the hydrogen generation rate decreases, the benefit of the larger diameter filter decreases.

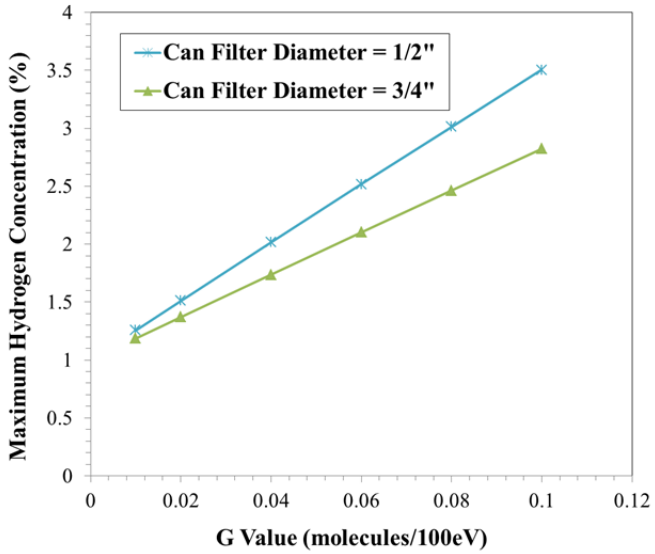

FIG 6. MAXIMUM HYDROGEN CONCENTRATION WITH FILTER DIAMETER VARIATION

The vertical spacing between the three cans as shown in Figure 7 indicates that the can spacing has little effect on the maximum hydrogen concentration for the spacings evaluated.

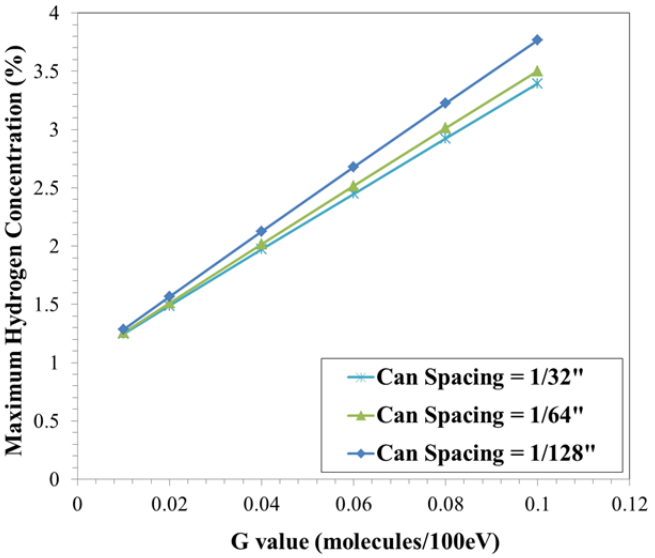

FIG 7. MAXIMUM HYDROGEN CONCENTRATION WITH VERTICAL CAN SPACING VARIATION

Figure 8 shows the results for the maximum hydrogen concentration as a function of inner can diameter. The outer can diameter is 4.75 inches. There is an increasing trend in the maximum hydrogen concentration as the inner can diameter

increases. This is due to the lower area for hydrogen diffusion around the sides of the cans to the upper recombiner. A significant increase in the maximum hydrogen concentration is seen when the inner can diameter increases from 4.4 to 4.5 inches. Values below 4 inches were not evaluated due to the volume of the inner can being too small to hold the specified oxide volume.

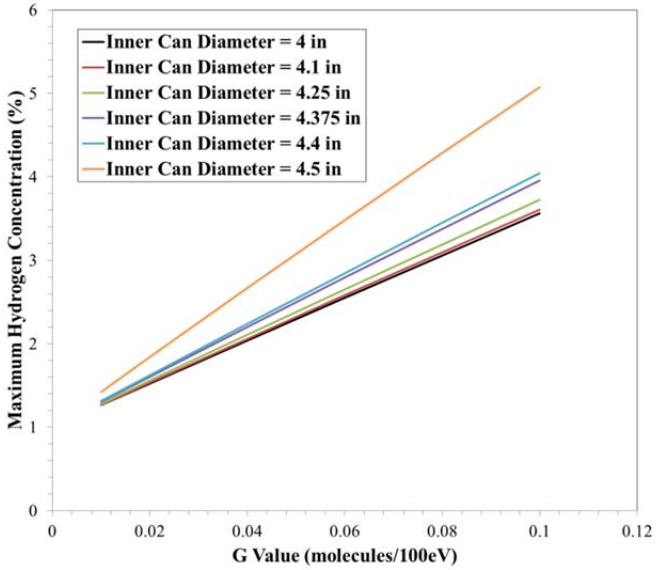

FIG 8. MAXIMUM HYDROGEN CONCENTRATION WITH INNER CAN DIAMETER VARIATION

As the outer can diameter is decreased from 4.875 inches to 4.625 inches, the curves for hydrogen concentration versus G-value increase, as seen in Figure 9. The cross sectional area available for hydrogen diffusion outside of bagging but inside the outer can significantly decreases when the outer can diameter is 4.625 inch or below (i.e. a diametric difference of 0.375 in. between the outer and inner can).

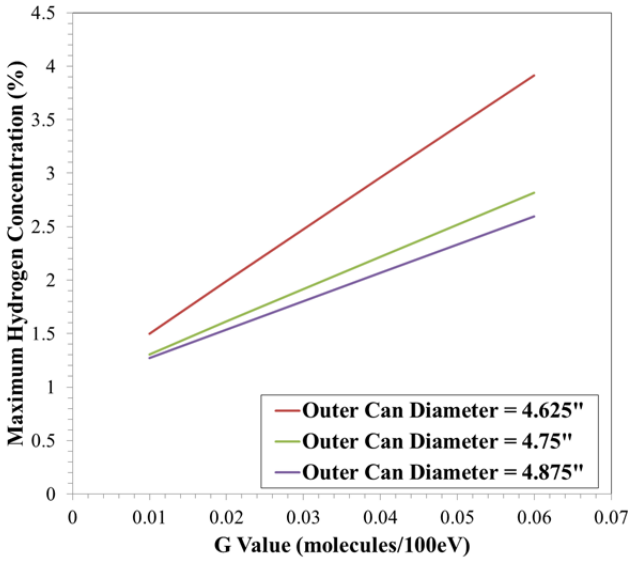

FIG 9. MAXIMUM HYDROGEN CONCENTATION WITH OUTER CAN DIAMETER VARIATION

The Comsol model does not explicitly consider the plastic bagging around the inner can. This plastic bagging will be irregular in shape which could facilitate a spiral diffusion path upwards in the outer can. With the moisture content of the oxide being 1.1 wt% or below, the outer and inner cans can be sized for a minimum diametric difference of 0.375 in. to mitigate the effects of the plastic bagging and ensure that the hydrogen concentration is below 4%.

CONCLUSIONS

Based on the data obtained from the steady state simulations, a maximum hydrogen concentration of less than 5.1% was obtained for all combinations of parameters evaluated. A gap must exist between the bag filter and the can above it in order to maintain a pathway for diffusion of hydrogen out of the inner canister. All hydrogen concentrations are less than 4% where the G-value is less than 0.058, which corresponds to plutonium oxide with moisture less than 1.1% by weight. In order to maintain sufficient cross sectional area for hydrogen diffusion within the outer can, the difference between the outer can diameter and the inner can diameter must be greater than 0.375 inches, while the moisture content of the oxide is 1.1 wt% or below. The simulations are valid for both air and nitrogen fill gas environments in the 9975 PCV.

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