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).

PVP2020-21682

EVALUATION OF HYDROGEN GAS GENERATION AND PERMEATION IN THE 9979 TYPE AF SHIPPING PACKAGE

Joshua P. Flach
Savannah River National Laboratory
Savannah River Site, Aiken, SC 29808
Email: joshua.flach@srnl.doe.gov

Paul S. Blanton
Savannah River National Laboratory
Savannah River Site, Aiken, SC 29808
Email: paul.blanton@srnl.doe.gov

Don S. Hoang
Savannah River National Laboratory
Savannah River Site, Aiken, SC 29808
Email: don.hoang@srnl.doe.gov

ABSTRACT

The 9979 Type AF Shipping Packaging is a cost-effective radioactive material package designed by Savannah River National Laboratory (SRNL) that consists of two primary components: a foamed outer drum for structural protection and an inner containment drum. The packaging was designed to transport Highly Enriched Uranium (HEU), Low Enriched Uranium (LEU), and other isotopes not exceeding a Type A quantity. These contents have the potential to generate flammable hydrogen gas during transport due to the degradation of hydrogenous materials (e.g. water vapor, plastics, etc) by high-energy alpha radiation. Since 10 CFR 71.43(h) prohibits the incorporation of packaging features explicitly designed for continuous venting, alternative justification was required to demonstrate that the requirements of 10 CFR 71.43(d) for negligible reactions between packaging components and contents were satisfied. An analysis was performed to demonstrate that the potential for hydrogen gas generation over a one-year period was limited by the effects of permeation through the packaging materials. The rate of hydrogen collection was evaluated for both the inner containment drum and the outer structural drum under 10 CFR 71.71 Normal Conditions of Transport (NCT). The analysis concludes that the Lower Flammability Limit (LFL) for hydrogen gas will not be reached in a one-year shipping period assuming a minimum void volume is maintained within the drum.

INTRODUCTION

The 9979 Type AF shipping packaging is a radioactive material packaging developed to ship Type A quantities of fissile materials (AF) including Highly Enriched Uranium (HEU) and Low Enriched Uranium (LEU). The packaging was designed to be sufficiently cost-effective to justify both one-time use disposal missions as well as multi-use applications. The package was first certified for use by the U.S. Department of Energy (DOE) in 2010 and is currently authorized for use in accordance with the Safety Analysis Report for Packaging (SARP)[1] under Revision 15 of the DOE Certificate of Compliance (CoC)[2].

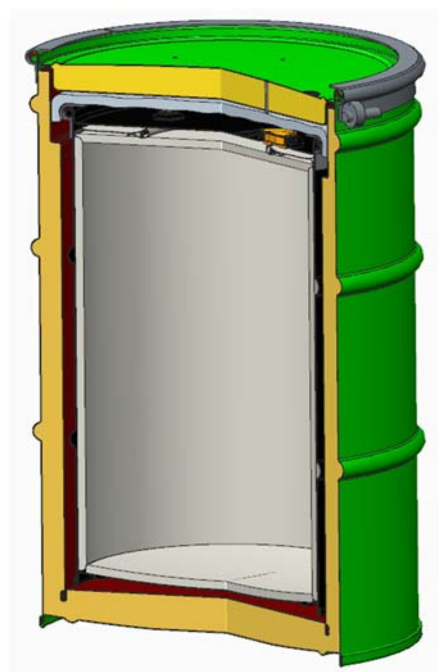

Figure 1: 9979 Type AF Radioactive Material Shipping Package

The 9979 is a composite packaging that consists of an outer drum assembly for structural protection and an inner drum assembly for containment. The outer drum assembly is composed of a commercial 55-gallon (208 L) drum, welded carbon steel liners, a polyurethane foam fill, and an insulating thermal blanket. The 55-gallon drum is sealed with a crescent-shaped Ethylene Propylene Diene Monomer (EPDM) seal and a

SRNL-STI-2020-00143

reinforced split-ring closure. Holes are drilled in the lid, bottom, and perimeter of the outer drum assembly to ensure that the foam vents during the 10 CFR 71.73, Hypothetical Accident Conditions (HAC)[3] pool-fire test. The inner packaging assembly is composed of a commercial 30-gallon (114 L) drum assembly and a thermal bag assembly. The inner containment drum is sealed with a crescent-shaped silicone seal and is closed with a smaller version of the reinforced split-ring used to secure the outer drum.

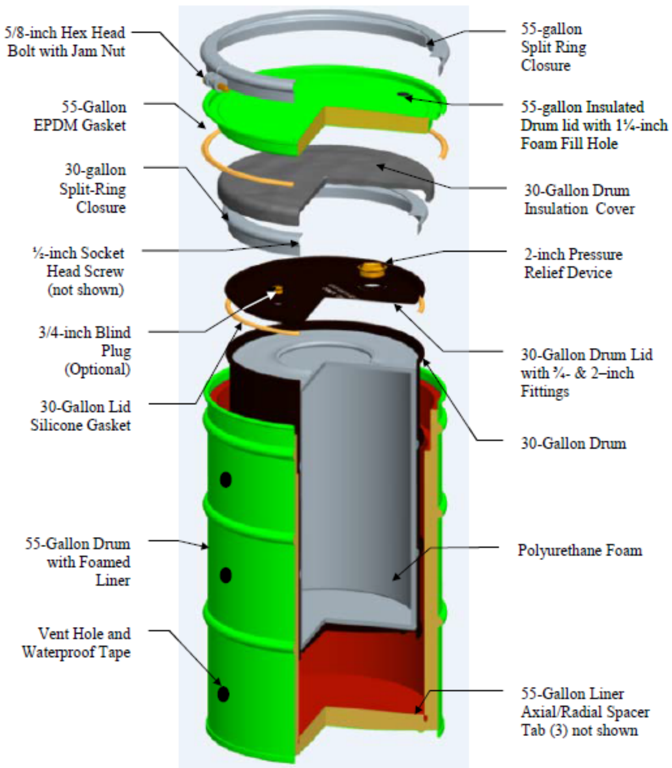

Figure 2: Annotated Exploded View of the 9979 Type AF Package

The radioactive contents of the 9979 release alpha, beta, gamma, and neutron particles during decay, which have the potential to break down the non-radioactive contents thereby releasing potentially flammable gasses into the containment drum volume. In order to meet the requirements of 10 CFR 71.43(h)[3], the decomposition of materials must be evaluated to determine that there will be no significant hydrogen build-up within the drum during the authorized shipping window. Accordingly, this study analyzes the potential hydrogen collection in the packaging assembly due to radioactive decay and the subsequent permeation of hydrogen from the drum to evaluate if a flammable gas mixture will develop over a one-year period.

NOMENCLATURE

A	Cross-Sectional Area
A_G	Avogadro's Number
A_{2m}	Normal Form Radionuclide Mass Limit
B_m	Normal Form Radionuclide Content Mass
d	Diffusivity
D	Energy Absorbed in Packaging Contents
D_0	Diffusion Pre-exponential Factor
E_a	Activation Energy
G	Hydrogen Gas Generation Constant Temperature
ΔH	Heat of Solution
K	Coefficient of Permeation
k	Conversion Factor
L	Length
n	Molecules
P	Pressure
q	Activation Energy
Q	Flow Rate
R	Ideal Gas Constant
S	Solubility
S_0	Solubility Constant
SA	Surface Area
t	Time
T	Temperature
v	Volume of 1 Mole of Gas at STP
V	Volume
V_G	Hydrogen Generation Rate
Φ	Permeability

APPROACH

The calculations for potential hydrogen gas generation and permeation within the packaging was done in accordance with NUREG/CR-6673[4] for the evaluation of hydrogen generation in TRU waste transportation packages. In this approach, four methods for hydrogen gas generation are considered: chemical reactions, thermal degradation, biological activity, and radiolysis. The effects of chemical reactions and biological activity on hydrogen generation can be neglected due to the highly controlled content envelope of the 9979 which precludes chemically reactive impurities and limits the moisture level within the package. Furthermore, thermal degradation and subsequent off-gassing of the 9979 contents is not considered because the temperatures within the packaging remain under 250ºF (121ºC) during 10CFR71.71 Normal Conditions of Transport (NCT)[3]. Assuming a content that emits a bounding decay heat of 3.5 Watts, the maximum internal temperature of the package is less than 190ºF (87.7ºC) under the maximum NCT solar insolation conditions. Consequently, the majority of hydrogen gas is produced due to radiolysis of the non-radioactive contents. Radiolysis products differ depending on the type of ionizing radiation; therefore, all radiation emitted by the 9979 contents is assumed to be alpha for conservatism. The bounding measure of radiolytic hydrogen gas generation (i.e. G value) is predominantly associated with alpha decay[4]. Each content envelope was evaluated to determine the maximum hydrogen gas generation within the 9979 during the shipping period. The effects of diffusion and permeation were then considered to determine the overall rate of hydrogen collection within the drum. This rate was then used to determine the minimum void volume required within the packaging to remain below the Lower Flammability Limit (LFL) of hydrogen gas.

HYDROGEN GAS GENENERATION

The 9979 packaging is authorized to ship three unique content envelopes of radioactive materials[2] in quantities lower than the maximum allowable activity for normal form, type A packages (i.e. an A_2)[3]. For applications in which more than one isotope is shipped concurrently, the aggregate of each isotope mass to A_2 ratio must be less than or equal to one (Eq. 1).

$$\sum_i \frac{B_m(i)}{A_{2m}(i)} \leq 1 \qquad (1)$$

The sum of ratios for envelope one is approximately 10; therefore, the package user is required to adjust the mass quantities accordingly to abide by the regulatory limits set in Eq. 1 and the total authorized radioactive material mass of 90,000 grams established in the CoC. For conservatism, only the isotope combinations with the highest potential decay heat are evaluated and the CoC mass limit is slightly exceeded to maximize decay heat (Table 1). The sum of ratios for content envelopes two (Table 2) and three (Table 3) sum to less than 1; therefore, no adjustments are required.

Content Envelope 1					
Authorized Isotopes	**Maximum Authorized Mass (g)**	**A_2 Limit (g)**	**Mass Ratio**	**Decay Heat (W)**	**Adjusted Decay Heat (W)**
Tc-99	1,428	1.43E+03	1.00E+00	8.00E-03	8.00E-03
Th-232	90,000	∞	0.00E+00	2.39E-04	0
U-232	5.00E-05	1.20E-03	4.15E-02	3.53E-05	0
U-233	16.6	1.67E+01	9.96E-01	4.70E-03	0
U-234	26.1	2.61E+01	1.00E+00	4.67E-03	0
U-235	350	∞	0.00E+00	2.14E-05	2.14E-05
U-236	2,500	2.50E+03	1.00E+00	4.43E-03	0
U-238	90,000	∞	0.00E+00	7.75E-04	7.75E-04
Np-237	76.9	7.69E+01	1.00E+00	1.60E-03	0
Pu-238	1.58E-03	1.59E-03	9.95E-01	8.91E-04	0
Pu-239	0.435	4.35E-01	1.00E+00	8.40E-04	0
Pu-240	0.119	1.19E-01	1.00E+00	8.53E-04	0
Pu-241	1.58E-02	1.58E-02	1.00E+00	5.02E-05	0
Am-241	7.69E-03	7.69E-03	1.00E+00	8.77E-04	0
Total			1.00E+01	2.80E-02	8.79E-03

Table 1. Content Envelope 1 Mass Limits & Adjusted Decay Heat

Content Envelope 2				
Authorized Isotopes	**Maximum Authorized Mass (g)**	**A_2 Limit (g)**	**Mass Ratio**	**Decay Heat (W)**
U-235	3796	∞	0	2.32E-04
U-238	15396	∞	0	1.33E-04
Total			0	3.64E-04

Table 2. Content Envelope 2 Mass Limits & Decay Heat

Content Envelope 3				
Authorized Isotopes	**Maximum Authorized Mass (g)**	**A_2 Limit (g)**	**Mass Ratio**	**Decay Heat (W)**
Tc-99	4.00E+00	1.43E+03	2.80E-03	0.0000224
Th-228	6.72E-09	3.33E-05	2.02E-04	1.80E-07
Th-230	3.84E-03	1.32E+00	2.92E-03	2.28E-06
Th-232	1.76E+00	∞	0.00E+00	4.68E-09
U-232	6.13E-08	1.67E+01	3.68E-09	0.00E+00
U-234	2.20E+01	2.61E+01	8.43E-01	3.94E-03
U-235	2.00E+03	∞	0.00E+00	1.22E-04
U-236	**1.72E+02**	2.50E+03	6.88E-02	3.04E-04
U-238	9.00E+04	∞	0.00E+00	7.75E-04
Np-237	**6.15E-02**	7.69E+01	8.00E-04	1.28E-06
Pu-238	1.22E-06	1.59E-03	7.69E-04	6.88E-07
Pu-239	5.63E-03	1.19E-01	4.73E-02	0.00E+00
Pu-241	3.41E-05	1.58E-02	2.16E-03	1.08E-07
Am-241	9.97E-07	7.69E-03	1.30E-04	0.00E+00
Total			9.69E-01	5.17E-03

Table 3. Content Envelope 3 Mass Limits & Decay Heat

The decay heat for each content envelope was used to calculate the rate of hydrogen gas generation using Eq. 2. Gas generation constants (G-values) of 1.60 × 10^4 molecules/MeV and 3.50 × 10^4 molecules/MeV for water and hydrocarbons respectively were sourced from NUREG/CR-6673 and, where materials were temperature dependent, adjusted using Eq. 3 for the bounding temperature conditions of NCT. To bound the potential non-radioactive contents within the 9979, gas generation at -40ºF (-40ºC) was assumed to be by water vapor only and gas generation at 77ºF (25ºC) and 153ºF (67ºC) was assumed to be by hydrocarbons only. Since all ionizing radiation is assumed to be alpha, the fraction of energy absorbed by each gas generating material is assumed to be 50%. The remaining energy is absorbed by the emitting contents or non-gas generating materials (e.g. metals)[4].

$$V_g = \frac{D \times G \times k \times v}{A_n} \qquad (2)$$

Where…

k = 6.24 × 10^{-12} MeV/J

v = 2.24 × 10^4 cm^3

A_g = 6.022 × 10^{23} molecules

$$G_{T_2} = G_{T_1} e^{\left[\left(\frac{E_a}{R}\right)\left(\frac{T_2 - T_1}{T_2 T_1}\right)\right]} \tag{3}$$

Where…

- G_{T1} = 1.60 × 10^4 molecules/MeV (water)
  = 3.50 × 10^4 molecules/MeV (hydrocarbons)
- E_a = 3 kcal/gmol
- R = 2.0 × 10^{-3} kcal/(K × mol)
- T_1 = 298K
- T_2 = 233K (-40ºF)
  = 298K (77ºF)
  = 340K (153ºF)

HYDROGEN GAS DIFFUSION & PERMEATION

Although diffusion of hydrogen gas is expected to be significant[5], the packaging assembly does not feature a constant leak geometry that can be easily analyzed. Each 9979 undergoes a hydrostatic leak test during fabrication to eliminate defective packagings and all Type AF packages are prohibited from incorporating venting features. As a result, any diffusion will be the result of unpredictable small gaps in the packaging seal, relief valve, and bottom lock seam. Whilst preliminary diffusion experiments on the 9979 by SRNL indicate that the packaging will leak significantly as the packaging assembly is cooled, this analysis conservatively ignores it.

Permeation of the hydrogen gas through the packaging materials occurs primarily through two avenues in the 30-gallon drum assembly: the silicone, crescent seal and the packaging walls. Smaller leak paths through the ¾ inch (1.9 cm) bung plug and 2 inch (5.1 cm) relief valve are conservatively not considered. The leak paths are largely identical in the 9979 outer drum assembly with exception to geometry and the polyurethane foam that lines the packaging walls. The 9979 is evaluated at three temperature conditions: NCT cold (-40°F / -40°C), NCT room temperature (77°F / 25°C), and NCT solar (153°F / 67°C). The NCT solar condition utilizes the maximum content and seal temperature calculated in the 9979 SARP. The intent of evaluating these three conditions is to determine the bounding rate of hydrogen collection.

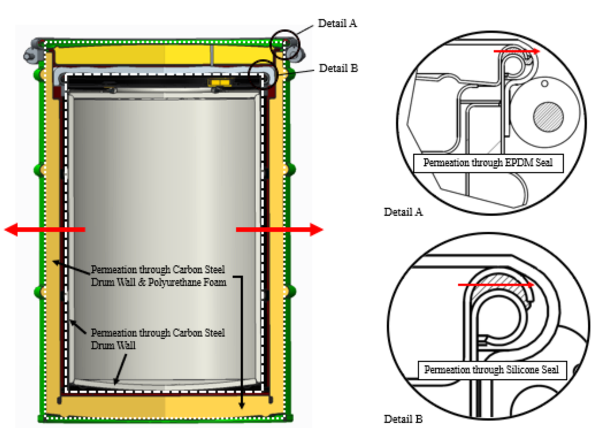

Figure 3: Hydrogen Permeation Paths for the 9979 Package

Hydrogen gas generated by radiolysis of the contents in the 30-gallon drum will increase the pressure within the drum. This internal pressure is the driver for gas permeation through the drum construction materials. The pressure within the drum was calculated as a function of hydrogen gas concentration by volume from 0% to the 5% NRC-recognized LFL[6] using the ideal gas law (Eq. 4) and Dalton's Law of Partial Pressures (Eq. 5).

$$PV = nRT \tag{4}$$

$$P_{total} = P_{air} + P_{H_2} \tag{5}$$

Hydrogen gas permeation through the drum seals of the 30-gallon and 55-gallon drum assemblies are calculated using Eq. 6. The crescent-shaped seal was evaluated as a rectangle profile with a thickness equal to the maximum crescent thickness. The permeation coefficient for each seal was taken from the Parker O-Ring Handbook at room temperature and was extrapolated for the full NCT temperature range based on known performance at other temperatures.

$$Q = \frac{KA(p_2 - p_1)}{L} \tag{6}$$

Where...

- A = 70.28 cm^2 (inner seal)
  = 114.01 cm^2 (outer seal)
- L = 1.85 cm (inner seal)
  = 2.54 cm (outer seal)
- K_{Si} = 1.18 × 10^{-6} cc cm / (cm^2 s atm) at -40°C
  = 4.95 × 10^{-6} cc cm / (cm^2 s atm) at 25°C
  = 1.10 × 10^{-5} cc cm / (cm^2 s atm) at 143°C
- K_{EPDM} = 8.00 × 10^{-8} cc cm / (cm^2 s atm) at -40°C
  = 4.00 × 10^{-7} cc cm / (cm^2 s atm) at 25°C
  = 1.00 × 10^{-6} cc cm / (cm^2 s atm) at 153°C

Hydrogen permeation through the carbon steel drum walls of the 30-gallon and 55-gallon drum assemblies are calculated using Eq. 7 - 11. Eq. 7 and 8 describe the diffusivity and solubility respectively of hydrogen gas within the metal. For this study, carbon steel is assumed to have the properties of elemental iron[8], which has been validated by the work of Kedzierzawaski[9]. Eq. 9 - 11 describes the permeability, flux, and flow rate of the hydrogen gas within the material respectively.

$$d = D_0 \times e^{\frac{-q}{RT}} \tag{7}$$

Where...

- D_0 = 1.60 × 10^{-3} cm^2/s
- Q = 1690 cal/mol
- R = 1.987 cal / (mol K)
- T = 233K (-40ºF)
  = 298K (77ºF)
  = 340K (153ºF)

$$S = S_0 \times \sqrt{p_{H_2}} \times e^{\frac{-\Delta H}{RT}} \quad (8)$$

Where...

S_0 = 2.98 cc_{STP} / (cc_{metal} $P_{atm}^{1/2}$)
ΔH = 6840 cal/mol
R = 1.987 cal / (mol K)
T = 233K (-40ºF)
= 298K (77ºF)
= 340K (153ºF)

$$\Phi = d \times S \quad (9)$$

$$Flux = \frac{\Phi}{L} \quad (10)$$

$$Q = Flux \times SA \quad (11)$$

The hydrogen permeation rates from all leak paths were then summed and subtracted from the generation rate to determine the net rate of hydrogen collection within the drum. The individual permeation rates of both carbon steel layers and the polyurethane foam in the outer drum were calculated independently and were combined utilizing Eq. 12. This approach is highly conservative since the outside of the drum is penetrated with holes during fabrication to act as vents during the HAC fire conditions. Although vented, this evaluation assumes that each layer is leak-free with exception to permeation.

$$Q_{total} = \frac{1}{\frac{1}{Q_{steel}} + \frac{1}{Q_{foam}} + \frac{1}{Q_{steel}}} \quad (12)$$

Figure 4 depicts the results from the calculations performed in Eq. 1 - 11. It is apparent that the permeation rate of the hydrogen gas from the drum is insignificant at the low end of the NCT cold conditions for the 30-gallon drum. This is primarily because the coefficient of permeation for the 9979 construction materials decreases steeply with a decline in temperature. As the package temperature increases; however, the permeation exceeds the generation rate at hydrogen partial pressures of 0.014 atm and 0.002 atm respectively. Hydrogen levels that exceed the LFL are unlikely at temperature conditions above room temperature.

The outer packaging does not feature the constant hydrogen generation rate that the 30-gallon drum does without contents. Instead, the flow rate of hydrogen gas into the 55-gallon drum assembly is dependent on the flow from the 30-gallon drum. In all cases, the permeation rate from the 55-gallon drum assembly is significantly lower than the permeation rate into the drum assembly. Because of this, a closer look at the required void volume of the 55-gallon drum is required.

REQUIRED VOID VOLUME FOR REGULATORY COMPLIANCE

An evaluation of the potential concentration of hydrogen gas within the packaging is required to ensure that the LFL is not reached under a one year shipping period. The limiting case for each content table is the NCT cold condition in which the reduced ambient temperature of -40°C greatly decreases the permeation from the packaging. The minimum required void volume for each content table is calculated using Eq. 13.

$$\frac{(V_{g,avg} - Q_{avg})t}{V_v} = 5\% \quad (13)$$

Where...

t = 3.15 × 10^7 seconds / year

The results of the void volume calculations are presented in Tables 4 and 5. No void volume in the inner drum is required for any content tables at temperatures above room (25°C) because the permeation rate exceeds the generation rate prior to 5% concentration. At the NCT cold conditions, the coefficient of permeation for the materials greatly decreases which largely negates the effects of permeation. Accordingly, this yields an 8.4% and 3.7% required void volume for content tables 1 & 3 respectively. The generation rate is significantly lower for content envelope 2; therefore, no void volume is required. Due to the large volume of the inner drum and payload limit of 200 lbs (90 kg), it is unlikely that the package can be loaded in a way that will violate these requirements.

Required Void Volume: Inner Drum			
Temperature (°C)	**Content Table 1**	**Content Table 2**	**Content Table 3**
-40	8.4%	0.0%	3.7%
25	0.0%	0.0%	0.0%
67	0.0%	0.0%	0.0%

Table 4. Void Volume Required in the 9979 Inner Drum

Although there is generally less hydrogen gas flow into the outer drum, the EPDM seal is far less permeable than the silicone seal present in the inner drum. This phenomenon results in more significant void volume requirements as demonstrated in Table 5. Despite these restrictions, there is a 25% void volume inherent to the 9979 packaging design consisting of the space between the outside of the inner drum and inside of the outer drum (Figure 3). This 25% void volume is more than double the highest void volume requirement for the outer drum; therefore, the outer drum will not reach the hydrogen LFL during a 1 year transportation period.

Required Void Volume: Outer Drum			
Temperature (°C)	**Content Table 1**	**Content Table 2**	**Content Table 3**
-40	0.5%	0.2%	0.5%
25	10.2%	0.0%	5.5%
67	4.7%	0.0%	0.0%

Table 5. Void Volume Required in the 9979 Outer Drum

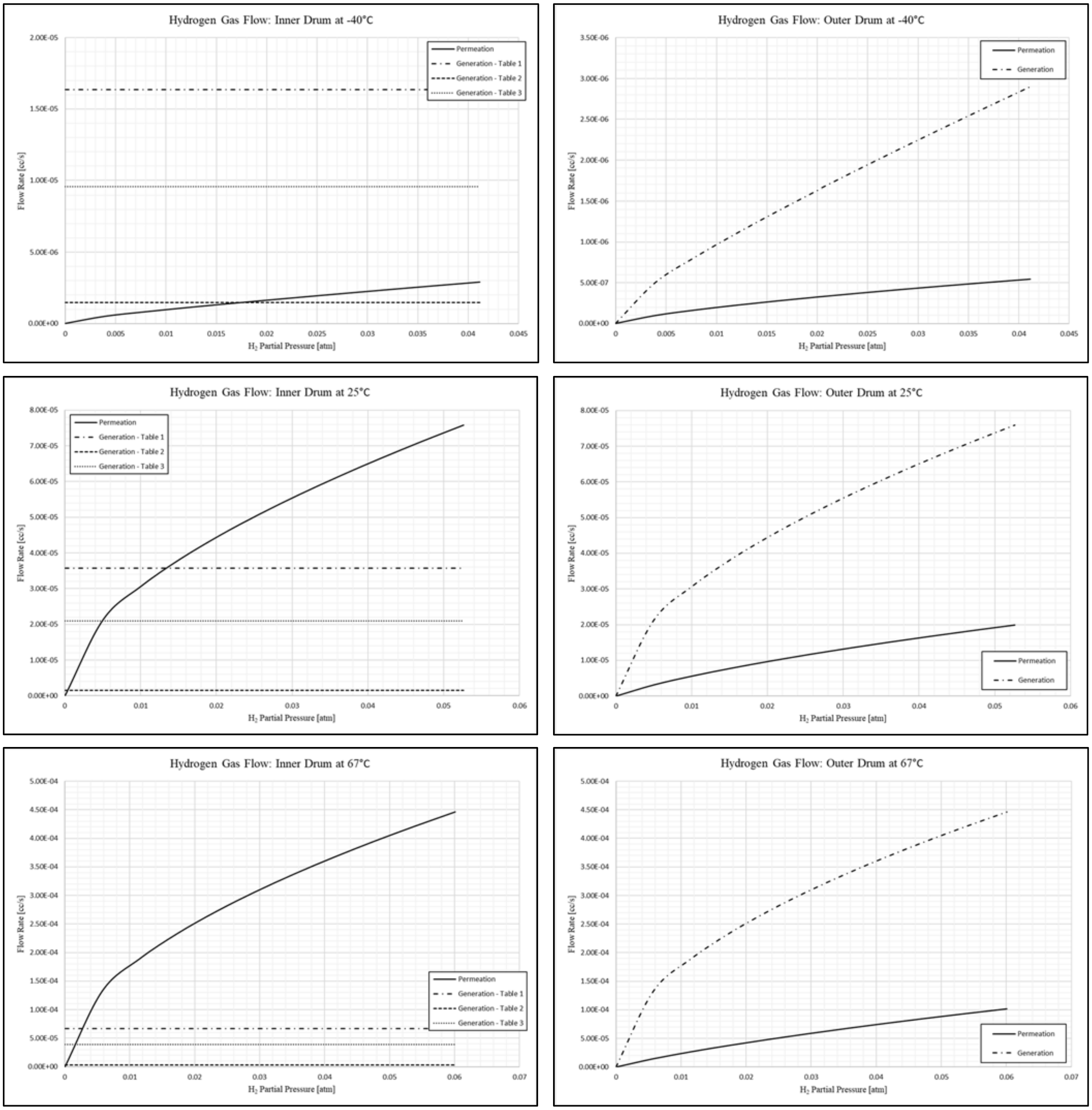

Figure 4: Hydrogen Balance within the Inner (Left) and Outer (Right) Packagings with Respect to Hydrogen Partial Pressure

CONCLUSIONS

The rate of hydrogen gas generation is primarily caused by decay heat of the contents; therefore, increasing the decay heat increases the gas generation rate. The results of this study present the rate of hydrogen gas generation within the 30-gallon drum and 55-gallon drum and the corresponding potential for permeation and diffusion caused by the pressure increase within the packaging. The required void volume required in the each assembly was calculated for each content table to ensure that the NRC-stipulated 5% hydrogen limit is not reached. Tables 4 & 5 summarize these minimum void volume requirements.

The void volume restrictions in Tables 4 & 5 ensure that the 9979 package will not reach a 5% hydrogen gas concentration within the (1) year shipping window assuming 9979 is shipped at the worst case scenario for Normal Conditions of Transport (NCT) of -40°C for one year following loading. No void volume restrictions are required under ambient or insolation conditions.

The void volume inherent to the outer drum is sufficient to prevent the LFL of hydrogen from being reached; therefore, no additional restrictions are required. The findings of this study apply only to shipping conditions and do not consider the effects of storage.

ACKNOWLEDGMENTS

The authors of this paper acknowledge the support of Neal Askew and the DOE-EM Packaging Certification Program (PCP) Review Team for their review of these calculations. Furthermore, Greg Sides, Donald Trapp, John Brookshire, and Doug Holiday of the SRNL High Pressure Laboratory were critical in conducting the experimental tests to determine the feasibility and repeatability of analyzing hydrogen gas diffusion.

REFERENCES

1. Blanton, P. S., 2018, "Safety Analysis Report for Packagings: Model 9979 Type AF Shipping Package," Revision 5.
2. Joanne D. Lawrence to Michael D. Budney, August 20, 2019, United States Department of Energy, Certificate of Compliance for Radioactive Materials Package: USA/9979/AF-96 (DOE).
3. "Code of Federal Regulations, Title 10, Part 71, Packaging and Transportation of Radioactive Material," Last modified December 23, 2019, https://www.nrc.gov/reading-rm/doc-collections/cfr/part071/
4. Anderson, B. L., Sheaffer, M. K., Fischer, L. E., May 2000, "NUREG/CR-6673: Hydrogen Generation in TRU Waste Transportation Packages."
5. Schlick-Hasper, E., Seidler, O., Goedecke, T., Kraume, M., (2015) "Measurement of Helium Leakage Rates through Closures of Dangerous Goods Packaging for the Assessment of Potentially Explosive Mixtures in Freight Containers," *Packaging Technology and Science*. Vo. 28, Pages 959-985.
6. Jordan, E. L., September 10, 1984, "Clarification of Conditions for Waste Shipments Subject to Hydrogen Gas Generation," SSINS#: 6835.
7. "O-Ring Permeation Coefficient Chart of Common Materials," Marco Rubber and Plastics, Accessed 07/26/2018, https://www.marcorubber.com/o-ring-permeation.htm.
8. N.R. Quick and H.H. Johnson, 1978, "Hydrogen and Deuterium in Iron, 49-506° C". Acta Metallurgica, Vol. 26, Pages 903-907.
9. P. Kedzierzawski, 1985, "Diffusivity of Hydrogen and Its Isotopes in Iron Alloys", Chapter 12 in Hydrogen Degradation of Ferrous Alloys, ed. R.A. Oriani, J.P. Hirth, and M. Smialowski, Noyes Publications, Park Ridge, New Jersey USA, p. 267.