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# Estimating Hydrogen Gas Concentration in the Void Spaces of Type AF Radioactive Material (RAM) Transport Packages

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**Abstract:** The generation of flammable gases, especially hydrogen, in radioactive material transportation packages is a safety concern that requires evaluation. This paper develops and solves the differential equations for the generation and accumulation of hydrogen gas from the radiolysis of water and hydrocarbons (i.e., polymeric content convenience bags) in a Type AF drum-type package under normal conditions of transport. The analysis includes the effects of the permeation of hydrogen out of the drum. In this example calculation, hydrogen permeation data from the literature, and hydrogen generation rate data (i.e., radiolytic G-values) for the contents are used to determine the concentration of hydrogen gas in the void spaces of the package as a function of time. The hydrogen concentration for the limiting normal transport condition (NCT) is calculated for carbon-steel and stainless-steel drums for one-year shipping periods as well as for storage times up to 5-years. The sensitivity of the results to the packaging materials, including the drum gasket material, is evaluated, and the time to reach 5 molar percent hydrogen is determined for several different cases. Additionally, guidance is provided related to ensuring conservative results are obtained when permeation is considered in radioactive material transport package gas generation calculations.

**Introduction:** All Type B and Type AF radioactive material packages are subject to a set of stringent requirements [1,2] on their thermal and structural performance under Normal Conditions of Transport (NCT) and Hypothetical Accident Conditions (HAC). These requirements are met through testing, analysis, or both, and are used to demonstrate the integrity of the containment systems of these packages. Very specific to Type B packages is the requirement that the containment vessel pass an annual leak test at its containment boundary to maintain certification. The requirement on Type AF packages is that there will be no release of contents under both NCT and HAC. This means that Type AF packages are not subject to an annual leak test requirement to maintain certification.

A Type AF package that contains water and/or hydrocarbons in addition to RAM contents has the potential to generate hydrogen gas through radiolysis. Since no annual leak test is required for these packages, which would require opening of the package, hydrogen gas could potentially build up to explosive concentrations over time as the package remains sealed for more than the one-year period that is typically associated with the Maximum Normal Operating Pressure.

This paper considers a common Type AF drum package design and evaluates the implications of hydrogen generation from the radiolysis of hydrocarbons and water to safety for both the short-term shipping periods (typically 1 yr) and long-term storage periods (5+ yrs). These determinations included the radiolytic generation of hydrogen within the package, as well as the permeation of hydrogen from the package. The calculations were performed by developing the governing differential equations for the generation and permeation of the hydrogen, and with the appropriate coefficients, solving the equations with Mathematica.

**Packaging Configuration and Components:** Figure 1 is the schematic of the nested drum arrangement for the Type AF package modeled. The main components consist of an inner 30 gal drum serving as containment with an overpack confined by an outer 55 gal drum. Both drums have inner steel liners. The drum closures consist of lids secured by bolted split-rings. There is polyurethane foam between the liners and drum walls serving both as thermal insulation and impact protection for the RAM contents. Also, there is an aluminum honeycomb cylinder between the contents and 30 gal drum lid providing additional impact protection. The drums are sealed with elastomeric seals between the drum chimes and split-ring closures.

The void spaces of the package are the volume inside the 30 gal drum's inner liner not occupied by contents and the volume between the inner 30 gal drum's wall and the 55 gal drum's liner.

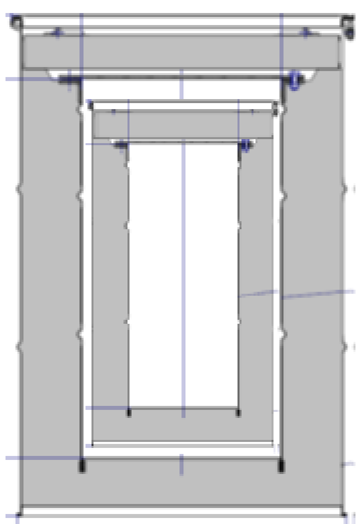

**Figure 1.** Common Type AF Package Configuration

**Mathematical Model:** The rate of hydrogen generation from water and hydrocarbons is a function of RAM contents decay heat, the type of radiation and the fraction of the radiation absorbed. The hydrogen generation rate from the radiolysis of hydrocarbons is also a strong function of temperature, while that of water is not. Equation (1a) is the expression for hydrocarbons and Equation (1b) is for water.

$$G_{HT2} = G_{HT1} e^{\frac{Ea}{R}\left(\frac{T2-T1}{T2*T1}\right)} \tag{1a}$$

Where $G_{HT1}$ is the hydrogen generation rate at temperature $T_1$, and $G_{HT2}$ is the generation rate at temperature $T_2$ in Molecules/MeV. Ea is the activation energy for hydrocarbons (3000 cal/mole), and R is the ideal gas constant (1.987 cal/K*mole).

$$G_{H2O} = 1.6E + 04 \;\; Molecules/MeV \tag{1b}$$

The volumetric hydrogen gas generation rate at STP for hydrogen generating contents consisting of water and hydrocarbon content convenience bags is given by Equation (2).

$$V_g = \frac{frad*E_D*(G_{H2O}+G_{HTi})*k*V}{N_A} \quad (cc_{STP}/s) \tag{2}$$

Where $E_D$ is the decay heat of the RAM contents, $f_{rad}$ is the fraction of the decay heat absorbed by the hydrogen generating contents, V is the volume of 1 mole of gas at STP and k is a unit conversion factor.

The permeation rate coefficient (STP), $\phi_M$, for the metal drum walls and lid of material, M, at a temperature, T, is given by Equation (3a).

$$\varphi_M = C0 * \left(\frac{\varphi_{M0}}{L}\right) * e^{\left(\frac{-C1*q\Delta H}{R*T}\right)} \quad (cc_{STP}*(atm)^{-1/2}/s*cm^2) \tag{3a}$$

Where L is the thickness; C0 and C1 are unit conversion factors; qΔH is the sum of the metal's activation energy of diffusion and heat of solution (for solubility); and $\phi_{M0}$ is the permeability constant of metal, M.

The corresponding volumetric flow rate (STP) of hydrogen through the metal is given by Equation (3b).

$$Q_M = \varphi_M * A * (\sqrt{p_2} - \sqrt{p_1}\,) \quad (cc_{STP}/s) \tag{3b}$$

Where $p_1$ and $p_2$ are the hydrogen partial pressures and A is the surface area for permeation.

The permeation rate coefficient (STP), $\phi_{SF}$, for elastomeric seals and foam is given by Equation (4a). Where K is the permeation constant of the material and t is the permeation thickness.

$$\varphi_{SF} = \frac{K}{t} \qquad (cc_{STP}*atm^{-1}/s*cm^2) \qquad (4a)$$

The corresponding volumetric flow rate (STP) of hydrogen through the elastomer is given by Equation (4b).

$$Q_{SF} = \varphi_{SF} * A * (p_2 - p_1) \qquad (cc_{STP}/s) \qquad (4b)$$

As before, $p_1$ and $p_2$ are the hydrogen partial pressures and A is the surface area for permeation.

Conservative assumptions were made in the analysis to try establishing upper-bounds on hydrogen gas accumulation in the void spaces of the package. Namely, these assumptions are:

(1) The only gas generated is hydrogen;
(2) The 55 gal drum is not vented;
(3) The permeation areas of the drums are based on liner surface areas. No additional credit is taken for the larger drum surface areas;
(4) A bounding room temperature gas generation rate of 4.1E+04 Molecules/MeV [3] is used for hydrocarbon material;
(5) All radiolysis is due to alpha absorption [3];
(6) The fraction of decay heat absorbed by hydrogen generating contents (i.e., water and/or hydrocarbons) is 50%;
(7) The polyurethane foam is assumed to have the same permeation rate as if it were solid polyurethane (Parker O-Ring Handbook) [4];
(8) The elastomer seal permeation coefficients are those given in the Parker O-Ring Handbook [4];
(9) There is sufficient hydrogen generating contents to generate hydrogen gas at a constant rate for 5 years; and
(10) The validity of the perfect gas law.

The 55 gal drum has two metal surfaces (drum and liner) plus a polyurethane foam layer at the top, bottom, and laterally that hydrogen permeates through. Also, there is a permeation path through the elastomeric seal at the closure of the 55 gal drum.

The 30 gal drum has two metal surfaces (drum and liner) plus a polyurethane foam layer at the bottom and laterally; and one metal surface at the top that hydrogen permeates through from the inner void volume ($V_1$) to the void volume between the two drums ($V_2$). Additionally, there is a permeation path through the elastomeric seal at the closure of the 30 gal drum.

With these assumptions, the rates of increase of the hydrogen partial volumes ($V_{H1}$, $V_{H2}$) in the void spaces is given by:

$$\frac{dV_{H1}}{dt} = (V_g - Q_{30D} - Q_{Iseal})\left(\frac{T_{max}}{T_{STP}}\right) \qquad (5a)$$

$$\frac{dV_{H2}}{dt} = (Q_{30D} + Q_{Iseal} - Q_{Oseal} - Q_{55D})(\frac{T_{max}}{T_{STP}}) \tag{5b}$$

Where $Q_{30D}$ is the total permeation rate of hydrogen from the contents void volume ($V_1$) of the 30 gal drum through its metals walls and foam to the void volume ($V_2$) between the drums. $Q_{Iseal}$ is the permeation rate through the inner seal to $V_2$ in parallel with $Q_{30D}$. $Q_{55D}$ is the total permeation rate of hydrogen from $V_2$ through the 55 gal drum's metal walls and foam to the environment. $Q_{Oseal}$ is the permeation rate through the outer seal to the environment in parallel with $Q_{55D}$.

**Analysis Results:** The drum and liner materials considered here are normalized 4130 carbon steel and 304 stainless steel. Table 1 gives the values $\phi_{M0}$ and $q\Delta H$ for these materials [5].

**Table 1. Permeation Parameters for Metal Package Components**

| Material | $\phi_{M0}$ ($cc_{STP}$*(atm)$^{-1/2}$/s*cm) | $q\Delta H$ (J/mole) |
|---|---|---|
| Normalized 4130 Steel | 6.53E-06 | 39,700 |
| 304 Stainless Steel | 2.34E-04 | 64,000 |

It was found that the most limiting NCT condition for the accumulation of hydrogen in the void spaces of the package is the regulatory thermal requirement that the package be evaluated for thermal steady-state in a 100$^{o}$ F environment with solar insolation. The content decay heats considered here range from 5 mW to 20 mW, which is a reasonable range for RAM contents of Type AF packages. The corresponding maximum component temperatures for this range of decay heats and the limiting NCT thermal condition is $T_{max}$ = 67$^{o}$ C for the drum package considered. The permeation constants [4] for polyurethane foam and seals at this temperature are given in Table 2.

**Table 2. Polyurethane Foam and Elastomeric Seal Permeation Constants**

| Material | Permeation Constant ($cc_{STP}$*atm$^{-1}$/s*cm)<br>At 67$^{o}$ C |
|---|---|
| Polyrethane | 7.04E-07 |
| Silicone | 1.10E-05 |
| EPDM | 1.00E-06 |

Equations (5a) and (5b) were solved numerically with Mathematica using parameter values corresponding to the 4130 carbon steel and 304 stainless steel in turn. The elastomeric material was the same in both cases.

Figure 2 and Figure 3 are 3-D plots of the hydrogen gas concentration (percent by volume) at the end of 1 year in the inner content void volume as a function of non-dimensional content decay heat ($E/E_0$) and non-dimensional inner volume restriction ($V/V_0$). The gold plane in the plot corresponds to the lower flammability limit (in air) of 5% hydrogen concentration by volume. The intersection of the hydrogen concentration surface with the gold plane defines the limiting combination of content decay heat and void space restriction to avoid the flammability limit of 5% hydrogen by volume. $E_0$

corresponds to the lower end of the range of decay heats considered (5.0 mW). $V_0$ is the unrestricted inner volume (71514 $cm^3$) for the drum package design considered.

These limiting combinations, for a one-year shipping window, of content decay heat and inner volume restriction are very similar for both 4130 carbon steel and 304 stainless steel. The limits on volume restriction vary essentially linearly over the range of decay heats considered. Specifically, when $E/E_0$ is equal to 1, the limit on volume restriction is ~0.45 $V_0$. For an unrestricted inner volume, i.e. $V = V_0$, the decay heat can be as high as ~1.6 $E_0$ and inner volume hydrogen concentration level will be below 5%.

Figure 4 is the plot of hydrogen concentration in void volumes $V_1$ (red) and $V_2$ (green) over a five-year storage period in a 4130 carbon steel drum package. The decay heat is 5 mW and there is no volume restriction in the contents volume, i.e. the void volume $V_1$ is essentially $V_0$ . The hydrogen concentration in $V_1$ will exceed the 5% limit over this storage period, but it will not be exceeded in $V_2$.

There is the possibility of drum surface contamination affecting the permeability of the drums. Figure 5 shows the hydrogen concentrations in $V_1$ and $V_2$ over this same five-year storage period except the permeability constant for the 4130 steel has been reduced by 50% to account for possible surface contamination. It is seen that the hydrogen concentrations are only marginally increased.

Figures 6 and 7 are the corresponding plots for stainless steel drum construction. The same conclusion can be reached, i.e. a 50% reduction in the permeability constant has only a marginal affect. However, for stainless steel, the hydrogen concentrations in both $V_1$ and $V_2$ will exceed the lower flammability limit of 5% hydrogen concentration in air.

Figure 8 is the plot of hydrogen concentration in void volumes $V_1$ (red) and $V_2$ (green) over a five-year storage period in a stainless steel drum package for a 50% reduction in the permeability of the elastomer seals. This has relatively greater affect on the void volume hydrogen concentration, but it is still under a 10% increase in both $V_1$ and in $V_2$.

The greater effect of seal permeability on hydrogen concentration in the void volumes, even though their permeation areas are smaller, is likely due to the difference in the way hydrogen permeates through elastomers as opposed to metals. The volumetric flow rate through elastomers is proportional to the linear difference between the inner and outer hydrogen partial pressures, while the volumetric flow rate through metal is proportional to the difference between the square roots of the inner and outer hydrogen partial pressures.

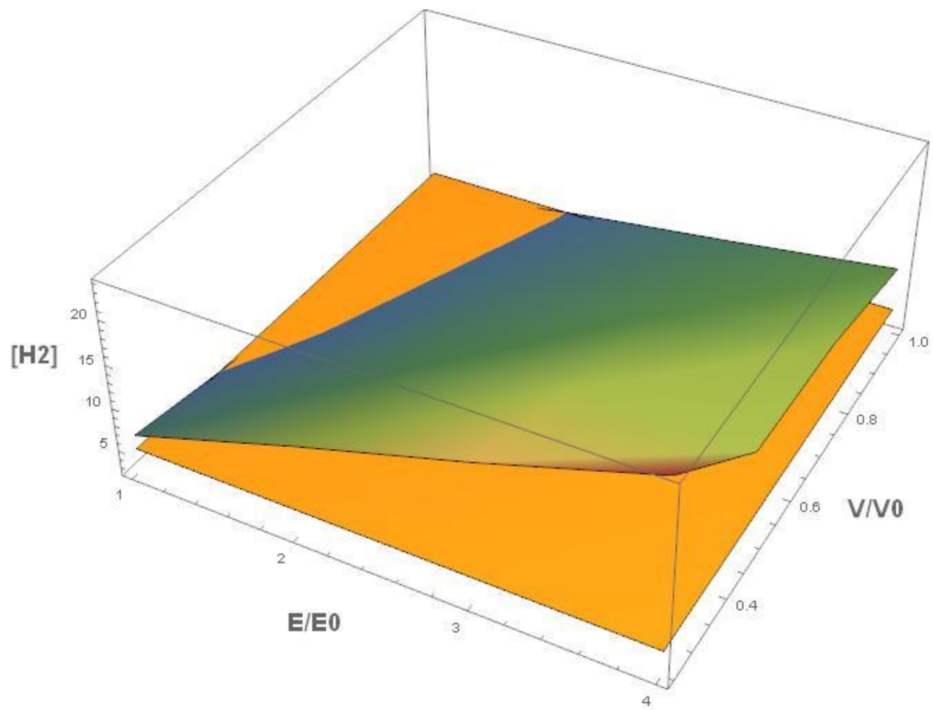


**Figure 2**. Flammability Limit for 4130 Carbon Steel Drums

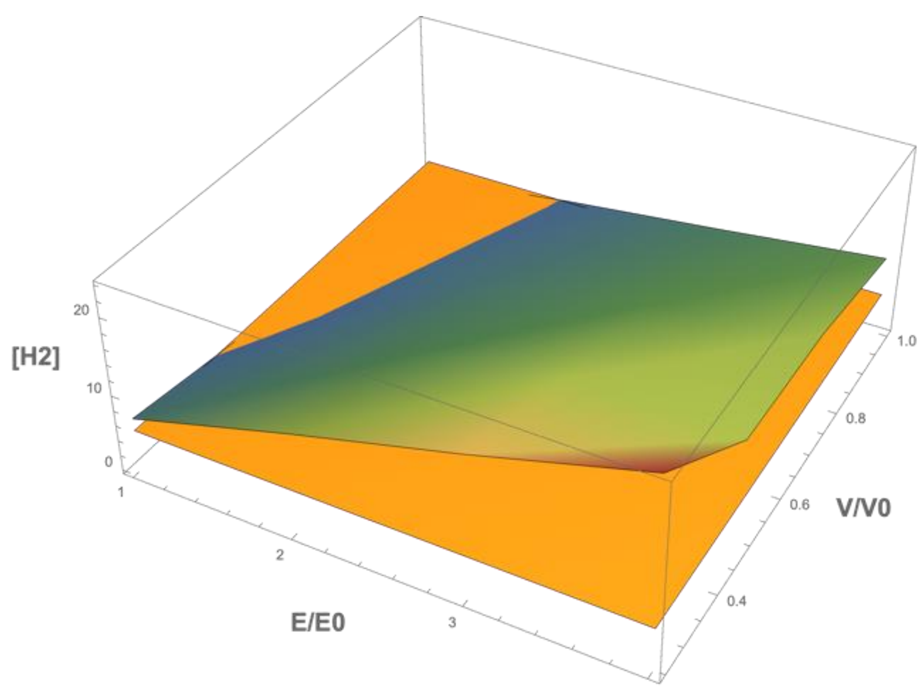


**Figure 3**. Flammability Limit for 304 Stainless Steel Drums

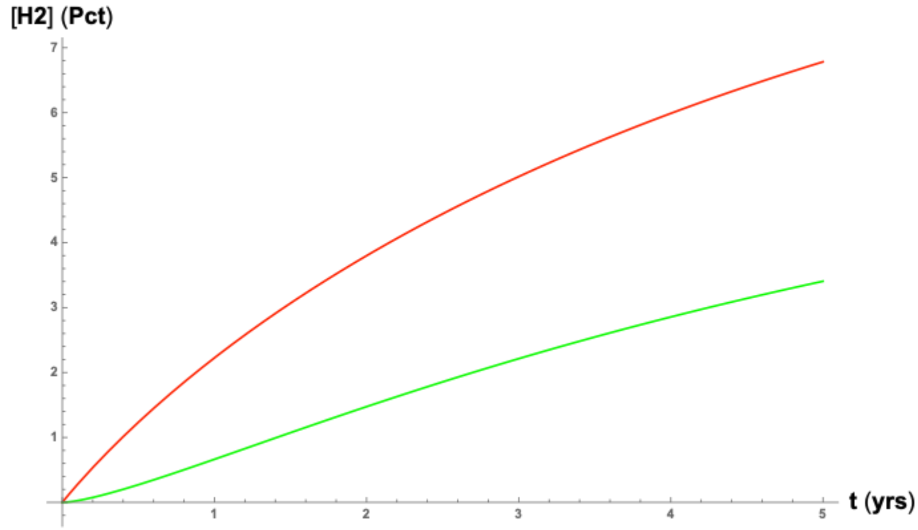


**Figure 4**. Hydrogen Concentration in V1 (red) and V2 (green) of 4130 Carbon Steel Drum Package Over 5-yr Storage Period (E=5.00e-03 watts, No volume restriction)

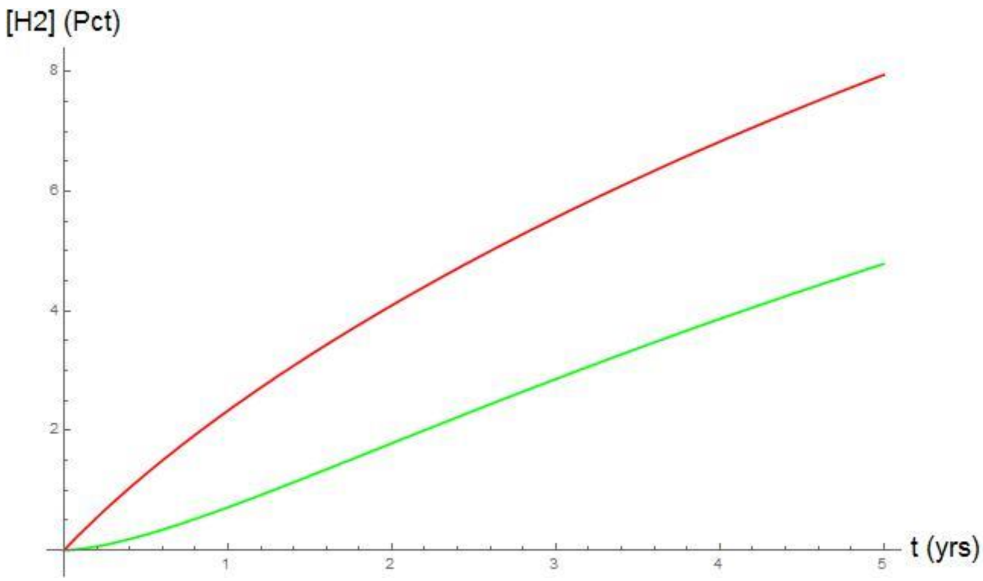


**Figure 5**. Hydrogen Concentration in V1 (red) and V2 (green) of 4130 Carbon Steel Drum Package Over 5-yr Storage Period (E=5.00e-03 watts, No volume restriction) with the Metal Permeability Constant Reduced by 50%

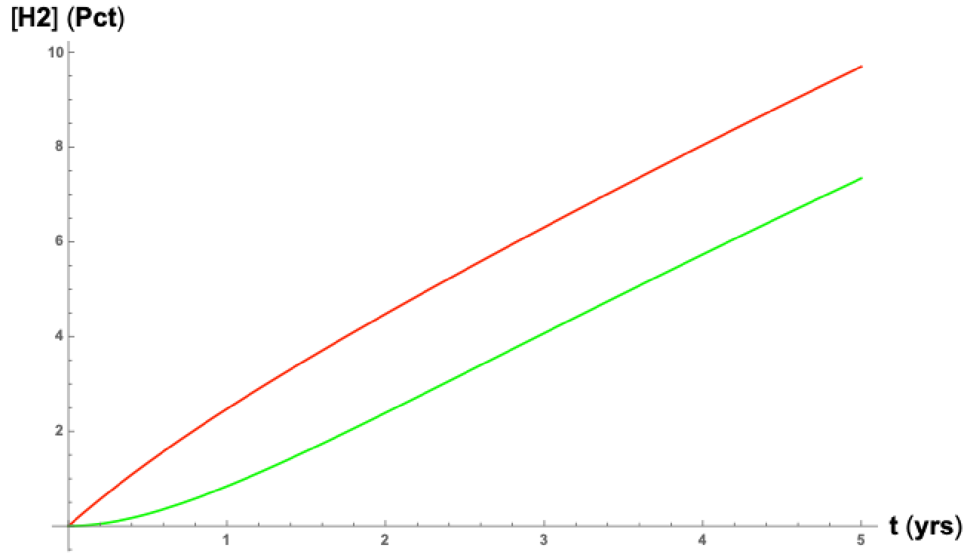


**Figure 6**. Hydrogen Concentration in V1 (red) and V2 (green) of 304 Stainless Steel Drum Package Over 5-yr Storage Period (E=5.00e-03 watts, No volume restriction)

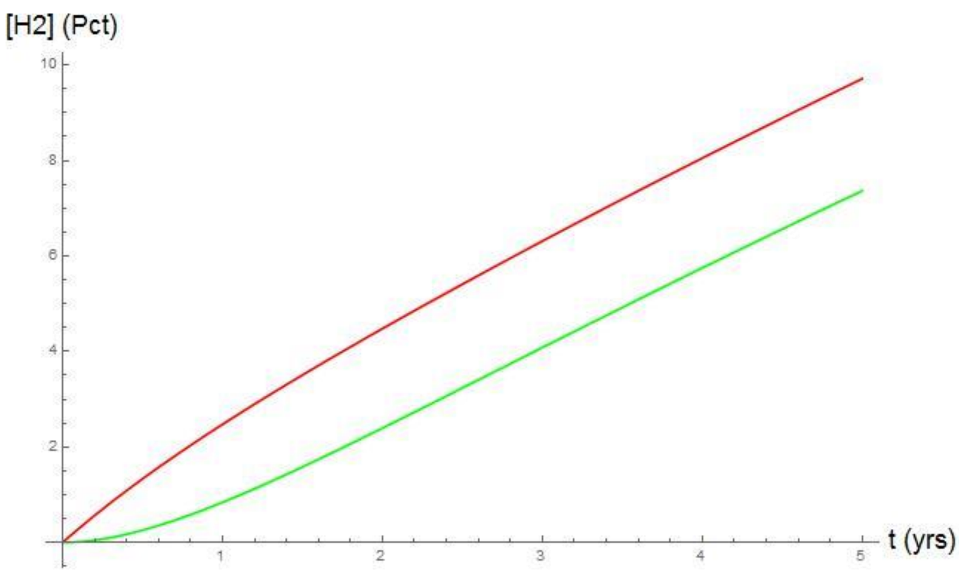


**Figure 7**. Hydrogen Concentration in V1 (red) and V2 (green) of 304 Stainless Steel Drum Package Over 5-yr Storage Period (E=5.00e-03 watts, No volume restriction) with the Metal Permeability Constant Reduced by 50%

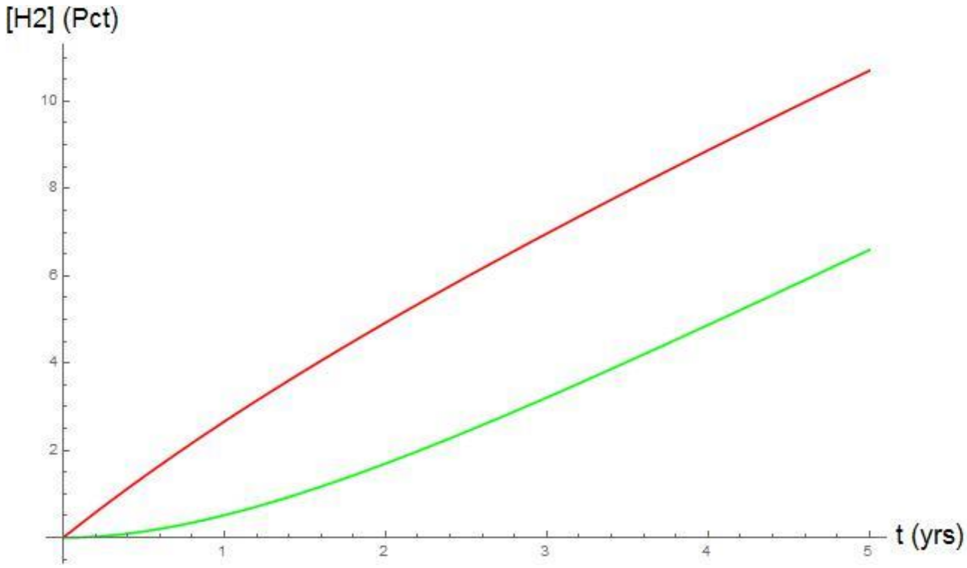


**Figure 8**. Hydrogen Concentration in V1 (red) and V2 (green) of 304 Stainless Steel Drum Package Over 5-yr Storage Period (E=5.00e-03 watts, No volume restriction) with the Elastomer Seal Permeability Constant Reduced by 50%

**Conclusion:** Differential equations governing the accumulation of radiolysis generated hydrogen gas in the void spaces of a Type AF drum packaging due to permeation were developed, then solved numerically. It was found that for NCT, the most limiting regulatory condition for the hydrogen generation and accumulation is the steady-state thermal condition of the packaging being in a 100$^o$ F environment with solar insolation.

We have shown that there is the potential for the hydrogen concentration in the void spaces exceeding the lower flammability limit of 5% during the one-year shipping period if the combination of content decay heat and content void volume restriction exceed certain limits.

Also, we have shown that even at the lowest decay heat considered and with no content void volume restriction, there is great potential for the 5% hydrogen concentration flammability limit to be exceeded after only a few years of storage.

Even when there is good confidence that the hydrogen concentration in the void spaces of a Type AF package will be below the 5% limit during the one-year period, this limit has the potential to be exceeded within a modest storage duration. Also, if the package is sealed prior to the shipping period, the 5% limit could potentially be exceeded during transport.

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