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A Permeation System for the Mitigation of Hydrogen Gas Accumulation Within Hazardous Material Packages

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Abstract:
We propose a new method to alleviate hydrogen (H_2) gas accumulation in hazardous material packages using a simple permeation system. The system accelerates H_2 permeation from an enclosed package while maintaining regulatory compliance. The proposed system can be used in new designs or for retrofits of commercial packages for shipping and storage, as well as other commercial applications where permeation is desirable. For example, it could be used as a replacement for pressure-relieving or loading openings of DOE radioactive materials packages thus eliminating other more complex or expensive mitigation techniques. Radioactive materials within packages can generate H_2 via radiolysis or chemical reactions, which poses significant challenges due to the flammability risk. IAEA regulations require that the H_2 content stay below the lower flammability limit (LFL) to eliminate this risk. Additionally, in many packages containing radioactive material, venting is not permitted to mitigate this risk. The combination of these two requirements can complicate design and maintenance of packages, requiring shortened shipping windows, the creation of an inerting atmosphere inside the package, or other mitigating actions. To address this issue, we have designed a compact permeation system comprised of a continuous gas permeable membrane (e.g., silicone) supported by a porous metal filtration material. The design prevents the release of radioactive material while allowing for the rapid permeation of H_2 through the membrane. Additionally, the cross-sectional area and membrane thickness can be tailored to align the permeation flow rate with the H_2 generation rate within the package such that the LFL is not exceeded over an indefinite duration. As an example, for the 9979 Type AF Package, analytical models and experimentation show that the permeation flow rate through the membrane quickly matches the generation rate even at low H_2 partial pressures, thereby removing the need for other more burdensome amelioration techniques. Removal of H_2 from radioactive material packages through permeation is a mechanism distinct from venting; therefore, it satisfies regulatory requirements on leaktightness of packages. This novel approach provides a simple and cost-effective solution to a longstanding problem within the radioactive materials packaging community.

Keywords: hydrogen permeation, 9979, radioactive materials package

1. Introduction

We propose a new method to alleviate hydrogen gas (H_2) accumulation within hazardous material packages using a simple permeation system. Hazardous materials, specifically for this work radioactive packages' contents, have the potential to generate H_2 via radiolysis of hydrogenous materials, or chemical reactions. The generation of H_2 has the potential to be hazardous if the hydrogen within the package exceeds the 5% lower flammability limit (LFL). As a result, both US

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[1] and IAEA **[CITATION?]** regulations require radioactive materials H_2 content to stay below this 5% limit**.** Additionally, features that allow continuous venting during shipping are prohibited [2].

A variety of mitigating design solutions are currently used in radioactive materials packaging to satisfy these requirements. However, each of these restrictions has notable disadvantages. One way to mitigate the H_2 generation is to restrict the shipping window. The drawback to this technique is that it impacts the loading, assembly, and shipping schedules, reducing operational flexibility. It can be difficult to implement because the minimum void volume within a package can be challenging to measure to verify compliance.

Another mitigation strategy is to sample and purge the flammable gas if it is close to or has exceeded the H_2 LFL. Both purging and measuring the flammable gas content requires work within a radiation/contamination area. An alternative to this would be to use an inerting gas within the package containment to dilute the oxygen content. Operations using this procedure can be expensive and time consuming.

Alternatively, hydrogen permeation through the packaging materials could also be credited. In one example, for storage containers, a permeation device was built into the structure of the container. The permeable membrane was immersed into the radioactive material, heating it, and thus boosting its permeability [3]. More simply, the permeation through the structural materials of the package could be calculated to show enough permeation occurs to avoid the 5% LFL.

The technique this paper proposes takes advantage of the permeation approach, but by using a specifically designed permeation device, titled the compact augmented permeation system (CAPS), the permeation reduced to a simple calculation over a single H_2 permeable membrane. The CAPS system can in many cases alleviate the need for other mitigation strategies such as restricted shipping windows, purging, or inerting. The way this proposed solution is designed, it can fit into standard sized holes use for other components in packaging such as pressure relieving devices. And, because permeation is not considered as venting (see for example reference [4]), the CAPS device avoids the venting prohibited for transport of radioactive materials.

2. Compact Augmented Permeation System

A picture of CAPS is shown in Figure 1, showing the main components of the system, with an exploded view in Figure 2. It consists of a structurally stiff supporting outer structure with holes to allow gases to pass in and out. Internally there is a polymer membrane, chosen because of its high permeability. This membrane is supported by a porous metal support material such as a sintered metal powder. Along with providing structural support to the membrane in the event of an impact, this porous material also acts as a filter, stopping larger particles such as dust or aerosolized radioactive particles, while allowing the smaller H_2 molecules to pass through to the membrane.

The permeable membrane geometry can be designed to a desired permeation rate. The membrane permeation rate is controlled by the material permeability, the membrane thickness, and the membrane surface area. To boost the membrane surface area a square wave has been imposed on the membrane. Other patterns, or modifications to this pattern, could increase the surface area, and therefore the H_2 flux through the membrane even further.

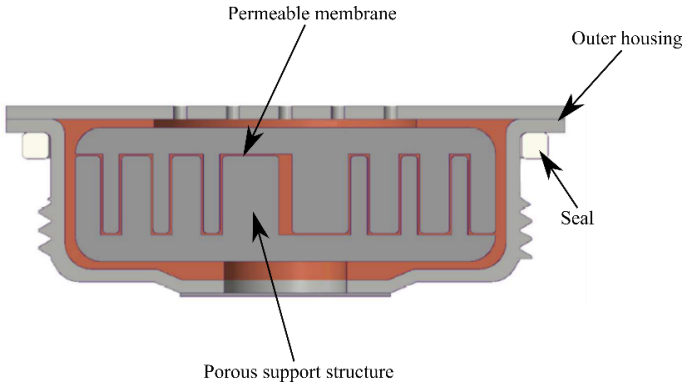

Figure 1: CAPS cross-sectional view.

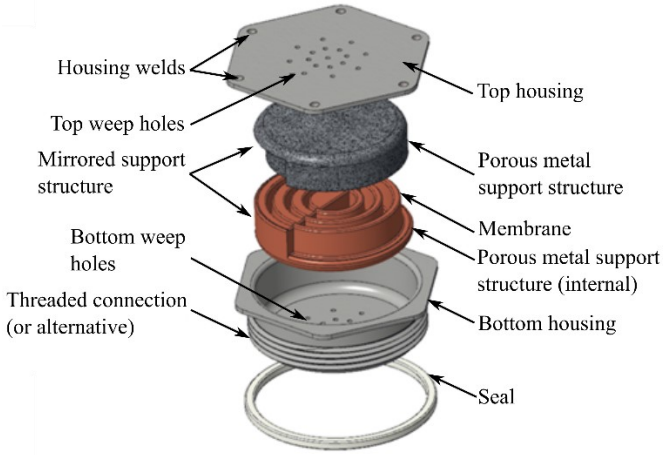

Figure 2: Exploded view of the CAPS assembly.

3. Package Permeation Analytical Model

3.1 Governing Equation

To model the permeation of H_2 through CAPS, implemented on a package, consider a hypothetical impermeable package (i.e. a control volume), with a permeable membrane as a part of its boundary. Assume that there is hydrogen generated inside of the control volume, at a known rate. Then to satisfy conservation of mass the H_2 collected within the control volume is

$$\frac{dn_c}{dt} = \frac{dn_g}{dt} - \frac{dn_p}{dt} \tag{1}$$

where n_c is the number of moles collected in the control volume, n_g is the amount of moles generated, and n_p is the amount of moles which has permeated out through the permeable membrane. $d/dt(\cdot)$ is the time derivative.

For shipping and storage conditions for radioactive materials packages, assume that the H_2 satisfies the ideal gas law, which is a valid assumption for the temperatures low pressures relative to the critical pressure and temperature of the gas. This is expressed as

$$PV = nRT \tag{2}$$

where P is the pressure, V is the volume, n is the number of moles, R is the ideal gas constant, and T is the temperature in Kelvins. The molar gas generation rate, dn_g/dt can be derived from Eq. (2), assuming normal temperature and pressure (NTP) conditions as

$$\frac{dn_g}{dt} = \frac{P_{NTP}}{RT_{NTP}}\frac{dV_g}{dt} \tag{3}$$

where dV_g/dt is the volumetric H_2 generation rate. Note that this value will be constant for a given temperature value for a radioactive materials package..

The H_2 collection rate in the system can also be derived from Eq. (2) assuming a constant void volume (the control volume) for the gas-filled system, giving that

$$\frac{dn_c}{dt} = \frac{V_{cv}}{RT}\frac{dP}{dt} \tag{4}$$

where V_{cv} is the control volume of the system. For the small amounts of gas generated for this problem, change in temperature is assumed to be negligible, and therefore T is treated as a constant.

The gas permeation is governed according to Fick's law [5]. This law requires intrinsic material properties, such as permeability, diffusivity, and solubility, to be applied. Using Fick's law and the experimentally measured temperature dependent permeability, the H_2 permeation through a membrane is

$$\frac{dn_p}{dt} = \frac{A\phi}{h}P \tag{5}$$

where A is the permeable membrane surface area, ϕ is the membrane permeability, and h is the membrane thickness. Replacing Eqs. (3) – (5) in Eq. (1) gives the governing differential equation of

$$\frac{A\phi}{h}P + \frac{V_{cv}}{RT}\frac{dP}{dt} - \frac{P_{NTP}}{RT_{NTP}}\frac{dV_g}{dt} = 0 \tag{6}$$

which for simplicity can be put into the form

$$\frac{dP}{dt} + c_1 P = c_2 \tag{7}$$

where

$$c_1 = \frac{RT}{V_{cv}}\frac{A\phi}{h} \tag{8}$$

$$c_2 = \frac{P_{NTP}}{T_{NTP}}\frac{T}{V_{cv}}\frac{dV_g}{dt}. \tag{9}$$

The solution to Eq. (7) is well known, and can be calculated using the integrating factor

$$M(t) = Ce^{\int c_1 dt} \tag{10}$$

to get that

$$P(t) = \frac{c_2}{c_1}(1 - e^{-c_1 t}) \tag{11}$$

Note that as $t \to \infty$, Eq. (12) converges to the steady state value of c_2/c_1. Also note, that while not functions of time, c_1 and c_2 are functions of temperature *T*. Built in is the assumption that the temperature is at a steady state value and is not a function of time. This assumption can be made because for a package of interest the temperature fluctuations throughout the day are slow compared to the rate of permeability of H_2 through the membrane.

3.2 Permeation Flow Through Membrane

The H_2 flow rate through the membrane is given by

$$Q(T) = AF(T) \tag{12}$$

where Q is the molar flow rate in mol/s, F is the permeation flux in mol/m^{2}s, and A and T are as previously defined. For the CAPS design presented in Section 2 the area is controlled by the pattern imposed on the membrane. In the specific case discussed here, it can be modified by changing the number of periods introduced in the square wave of the membrane.

The permeation flux, as a function of temperature, is given by

$$F = \phi(T)\frac{P_{H_2}(T)}{h} \tag{13}$$

where $P_{H_2}(T)$ is the partial pressure of H_2 as a function of temperature, and h is the membrane thickness. $P_{H_2}(T)$ within a control volume, as a function of volume percent, can be derived from the relationships for the ith species in a gas as

$$v_f = \frac{v_i}{v_{tot}} = \frac{p_i}{p_{tot}} \tag{14}$$

where v_f is the percent volume fraction, v_i is the volume of the *i*th species of gas, v_{tot} is the total volume, p_i is the partial pressure of the *i*th species of gas, and p_{tot} is the total pressure in the control volume. Assuming that the control volume contains only air and H_2 then the percent volume fraction $v_{f_{H_2}}$ for H_2 can be calculated as

$$v_{f_{H_2}} = \frac{v_{H_2}}{v_a + v_{H_2}} \tag{15}$$

where v_a is the volume of air, indicated by the subscript a. Combining Equations (14) and (15) provides the relationship

$$p_{H_2} = \frac{v_f}{1 - v_f} p_a \tag{16}$$

which can be used to calculate the H_2 partial pressure p_{H_2} as a function of volume fraction and atmospheric pressure.

Gay-Lussac's law allows for the incorporation of temperature dependence. According to this law, for two different temperatures, $P_1/T_1 = P_2/T_2$. This relationship gives that

$$P_2 = \frac{T_2}{T_1} P_1 \tag{17}$$

which, when combined with Eq. (16) gives the temperature dependent partial pressure of H_2 as

$$p_{H_2}(T) = \frac{v_f}{1 - v_f}\frac{T}{T_1}p_a. \tag{18}$$

Subbing Eq. (18) into Eq. (13) and Eq. (13) into Eq. (12) provides the H_2 flow rate through the membrane, of

$$Q = \frac{A\,\phi(T)}{h}\,\frac{v_f}{1 - v_f}\frac{T}{T_1}p_a. \tag{19}$$

Equation (19) will calculate the permeation flow rate through the membrane as a function of temperature.

4. Model Experimental Validation

Testing of the prototype shown in Figs. 1 and 2 validated the model given in Eqs. (8), (9), and (19). Information on the test article geometric and material parameters is provided in Table 1. The permeability of the 26A durometer silicone was extrapolated from previously measured permeabilities for 40A and 70A durometer silicones. These permeabilities were measured using the apparatus and procedures described in reference [6]. Silicone permeability, which follows an Arrhenius relationship as a function of temperature, was calculated using the relationships

$$\phi_{40A}(T) = 5.635 \cdot 10^{-8} e^{0.0193(T - 273.15)}$$

$$\phi_{70A}(T) = 3.467 \cdot 10^{-8} e^{0.0193(T - 273.15)}$$

$$\phi_{26A}(T) = \frac{\phi_{70A}(T) - \phi_{40A}(T)}{70 - 40}(26 - 40) + \phi_{40A}(T) \tag{20}$$

Table 1: Test article material and geometric parameters.

Material	Durometer	Membrane Area	Thickness
Silicone	26A	7.522E-3 m^2 (11.66 in^2)	0.254 mm (0.01 in)

CAPS was tested by measuring the amount of helium gas permeated through the system and comparing to that predicted by the analytical model. Figure 3 shows a diagram of the test setup used to test the permeation rate of the prototype and Figure 4 shows a picture of the physical hardware. The void volume for this test setup was approximately 2.43×10^{-6} m^3. To perform the test CAPS was placed inside of a bell jar and both upstream and downstream of CAPS was evacuated. A mass spectrometer located downstream of CAPS was used to measure the amount of helium that

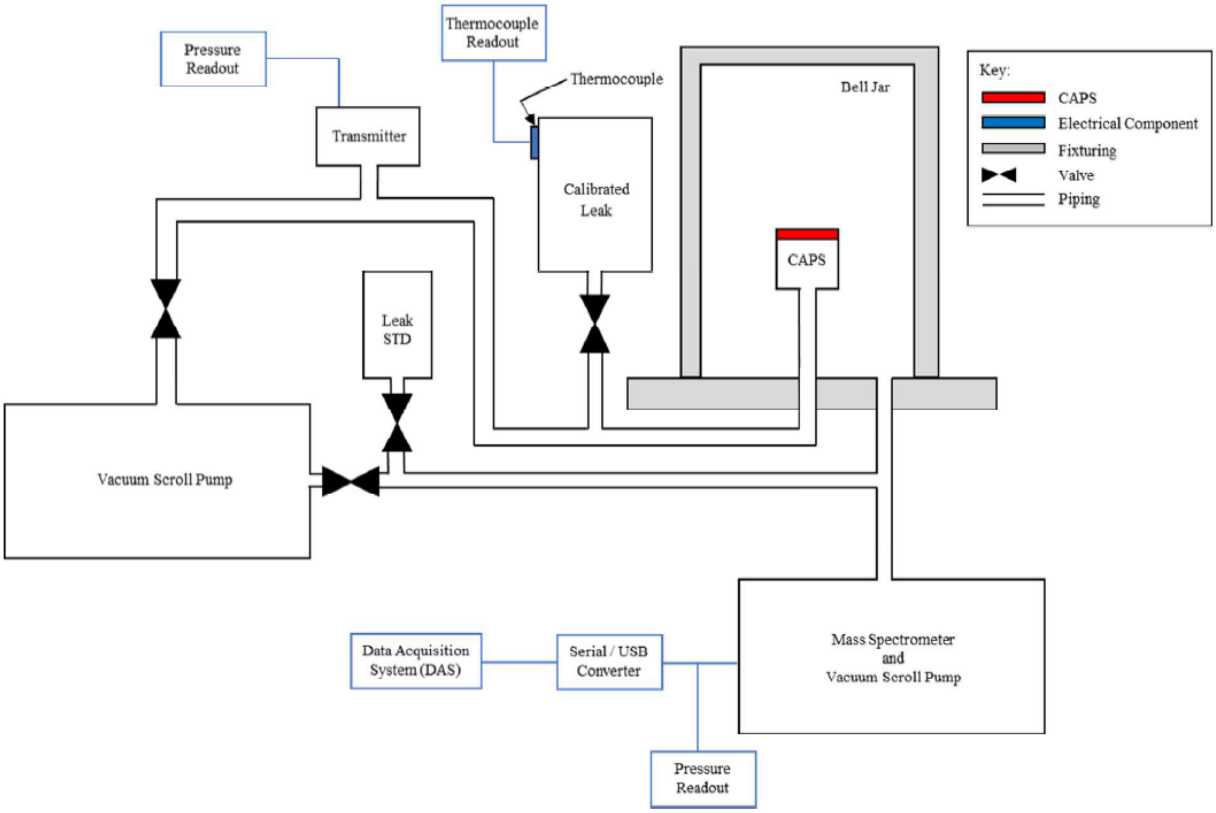

Figure 3: Diagram of experimental test setup for validating the analytical flow rate models.

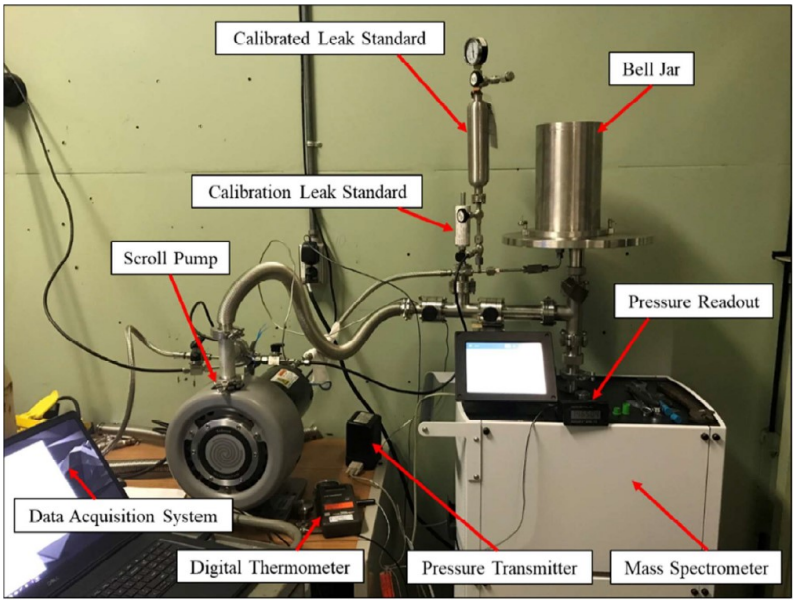

Figure 4: Experimental test set up for CAPS permeation testing.

permeated through the system. The mass spectrometer was calibrated using a helium leak standard downstream of CAPS. After it was calibrated this leak standard was turned off, and then a calibrated helium leak was released upstream and allowed to flow into the cavity behind CAPS. The

amount of helium permeated was then measured as a function of time. Note that although the permeability was measured using H_2 and the test was performed using helium, the permeability of H_2 is 1.5 times that of helium [7], so it is very simple to convert from one gas to another.

Figure 5 shows a comparison of the analytically predicted flow rate compared to the experimentally measured flow rate. The closeness of these results verify that the analytical model is accurately modeling the permeated gas through the membrane. Even though the permeation generation rate from the leak standard is very low, approximately 4.5E-5 cc/s, the partial pressure differential is enough to cause saturation of the membrane within approximately 3 hours, causing the permeation flow rate to match the generation rate. At this leakage rate the volume fraction is approximately 0.6%.

5. Example Application – 9979 H_2 Gas Generation

As an example application for the use of CAPS, consider the 9979AF radioactive materials shipping package. The 9979 is a low cost disposable type AF package mostly used to ship miscellaneous radioactive waste, but is also approved for some low and high enriched fuels, and some special form containers**.** This package was chosen as an example because, for some of the approved contents, the H_2 generation rate mitigation requires sampling or purging after 180 days as well as minimum limits on void volume [8]. The use of a permeation device, such as CAPS, could potentially allow for these restrictions to be removed.

Consider H_2 generation within a hypothetical 9979AF package with unlimited hydrogenous materials (i.e. no reduction in H_2 generation over time). The volumetric H_2 generation in cc/s is described by the equation

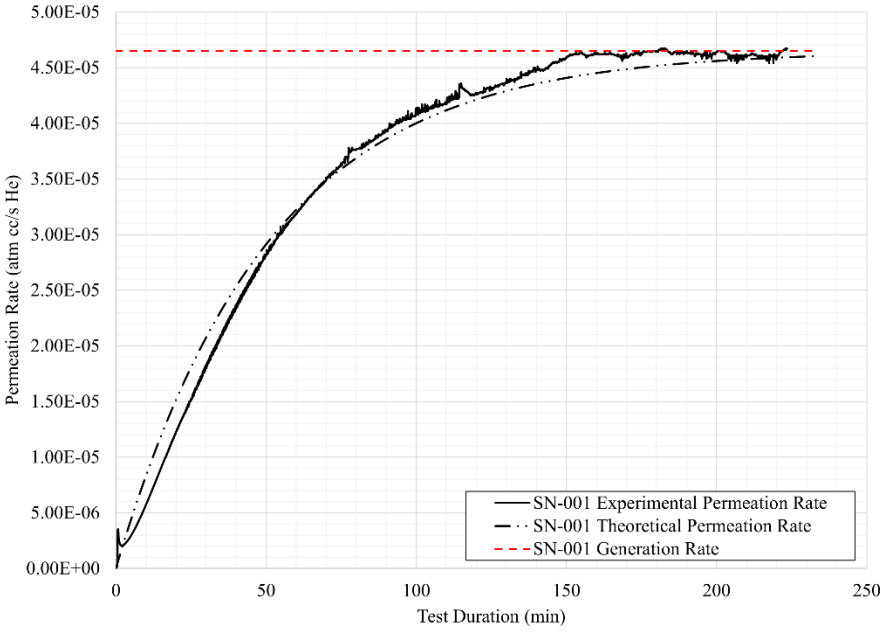

Figure 5: CAPS prototype experimental test results.

$$V = \frac{0.5DG(T)kv}{A_g} \tag{22}$$

where

$$G(T) = \begin{cases} G_{h_2o} & -40 \leq T \leq -15.6\,℃ \\ G_{hc}(T) & -15.6 < T \leq 67\,℃ \end{cases} \tag{21}$$

$$G_{hc}(T) = G_{T_1} e^{\left[\frac{E_a}{R_g}\frac{(T-T_1)}{T\cdot T_1}\right]}. \tag{23}$$

In Eqs. (21) – (23) $G_{hc}(T)$ represents the H_2 generated by hydrocarbons (e.g. foam or plastic within the package). G_{h_2o} is constant with respect to temperature and dominates at low temperatures. Its value is provided in Table 2. In Eq. (22) D is the decay heat, k is a conversion factor, v is the volume of 1 mole of gas at standard temperature and pressure, and A_g is Avogadro's number. In Eq. (23) E_a is the activation energy, $R_g$is the ideal gas constant, and T_1 is a reference temperature, chosen here as the standard temperature. Units, and values (when available without loss of generality), are provided in Table 2. The decay heat D is dependent on the package contents. For the

Table 2: Units and values for variables in Eqs. (22) and (23).

	G_{h_2o}	D	k	v	A_g	G_{T_1}	E_a	R_g	T_1	T
Unit and Value	1.6E4 molecules /MeV	W	6.24E12 MeV/J	2.24E4 cc	6.022E23 molecules	Molecules /MeV	3 kcal /gmol	2E-3 kcal/$K \cdot mol$	298.15 K	K

9979AF package the bounding total decay heat is 11.8 mW [9].

Figure 6 shows the predicted H_2 permeation flow rate as a function of time, for $T_{stp} = 25$ ℃, assuming the same void volume as that used in the experimental setup. Note that the flow rate reaches the generation rate in approximately 25 minutes. At this temperature the H_2 gas takes up approximately 0.6% of the void volume, significantly lower than the 5% LFL.

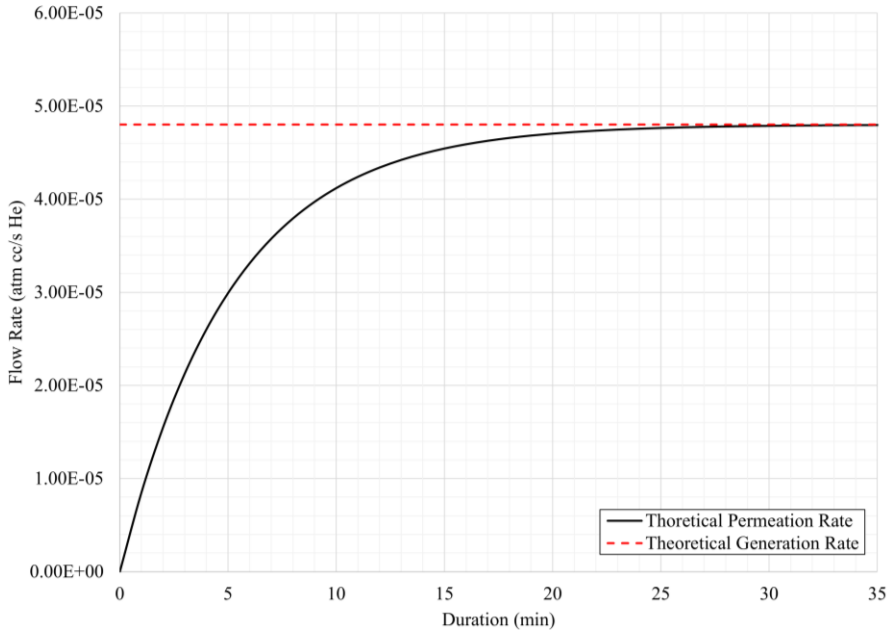

Figure 6: Predicted theoretical permeation flow rate through test CAPS on hypothetical 9979AF package.

As previously noted and captured in Eq. (20) the silicone permeability is a function of temperature, with the permeability following an exponential decay as temperature decreases. This suggests that the limiting flow rate for H_2 permeation will occur at low temperatures. Figure 7 presents the percent volume fraction and safety factor as functions of the temperature for the steady state permeation flow rate, over the temperature range where the gas generation rate is defined in Eq. (21). It shows that indeed the percent volume fraction increases at low temperatures, to a maximum of 1.2% volume fraction. The safety factor, calculated as 5% (for the LFL) over the percent volume fraction, shows that even at this low temperature there is a safety factor of approximately 4, providing confidence that the H_2 gas within CAPS will permeate out of the system over the temperature range of interest.

This analysis suggests that using the CAPS design as presented here, even in the worst-case scenario CAPS would prevent the LFL from being reached, thus potentially mitigating the need for the 180 day shipping window. Additionally, in this analysis an extremely small void volume was assumed, which would be small even for tightly packed packages, suggesting that limitations on the void volume could also be removed.

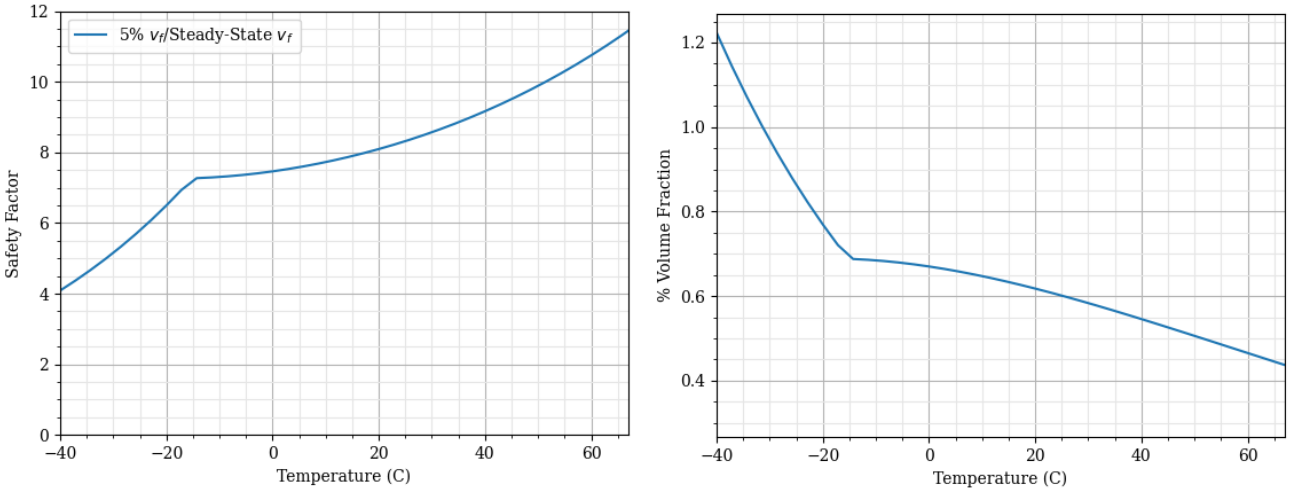

Figure 7: Safety factor and % volume fraction as a function of temperature, for steady state H_2 permeation out of a hypothetical 9979 package.

6. Conclusions

This work has presented a compact augmented permeation system designed to allow for the permeation of H_2 gas out of an enclosed volume. It has presented a mathematical model to predict the flow out of enclosed cavities using this system and presented experimental results validating this model. Finally, an example implementation, on a 9979AF package, was modeled, to show that using CAPS could potentially be one way to alleviate the H_2 gas generation and reduced shipping windows for this package. Along with potentially ameliorating shipping window issues for transportation packages, CAPS could also be deployed on packages used for long term storage of radioactive materials, or possibly for other chemical containers that have contents that outgas, which may have similar H_2 generation problems.

7. References

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