

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 (H₂) gas accumulation in hazardous material packages using a simple permeation system. The system accelerates H₂ permeation from enclosed packages 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. H₂ generation occurs via radiolysis in radioactive materials packages. This poses significant challenges due to the flammability risk. IAEA regulations require that the H₂ content stay below the lower flammability limit (LFL) to eliminate this risk. Additionally, in many packages containing radioactive material, continuous venting is not permitted. The combination of these two requirements complicates the design of packages, requiring shortened shipping windows, an inerting atmosphere within the package, or other mitigating actions. To address this, we propose 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 H₂ through the membrane. It can be tailored to prevent H₂ accumulation by aligning the permeation flow rate with the H₂ generation rate. Analytical and experimental models show that the permeation flow rate through the membrane quickly matches the generation rate even at low H₂ partial pressures, thereby removing the need for other more burdensome amelioration techniques. 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 (H₂) accumulation within hazardous material packages using a simple permeation system. Hazardous materials, specifically for this work radioactive materials package' contents, have the potential to generate H₂ via radiolysis of hydrogenous materials, or chemical reactions. The generation of H₂ has the potential to be hazardous if the H₂ within the package exceeds the 5% lower flammability limit (LFL). As a result, both US [1, 2] and IAEA [3] regulations require radioactive materials H₂ content to stay below this 5% limit. Additionally, features that allow continuous venting during shipping are prohibited [1].

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 H₂ generation is to restrict the shipping window and implement a minimum void

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volume within the package. 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 for compliance verification.

Another mitigation strategy is to sample and purge the flammable gas if it is close to or has exceeded the H₂ LFL. Both options 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, H₂ permeation through the packaging materials could also be credited. For 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 [4]. Traditionally, these types of devices are designed to be large to increase the available surface area for permeation. More simply, the permeation through the structural materials of the package could be calculated to show enough permeation occurs to avoid the 5% LFL. However, this method is typically only viable for contents generating smaller quantities of H₂.

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 from a system can be significantly increased beyond what is traditionally possible. The permeation is also reduced to a simple calculation over a single H₂ 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 used for other components in packaging such as pressure relieving devices and, because permeation is not considered as venting (see for example reference [5]), the CAPS device remains viable for transport of radioactive materials where continuous venting is prohibited.

2. Compact Augmented Permeation System

Figure 1 shows a cross-section of CAPS along with an exploded view. CAPS consists of a 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. A porous metal material such as a sintered metal powder, supports this membrane. Along with structural support to the membrane in the event of an impact, this porous material also acts as a filter, stopping larger particles such as aerosolized radioactive particles, while allowing the smaller H₂ 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 H₂ flux through the membrane even further.

3. Package Permeation Analytical Model

3.1 Governing Equation

To model the permeation of H₂ 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 H₂ is generated inside of a control volume, at a known rate. Then to satisfy conservation of mass the H₂ collected within the control volume satisfies

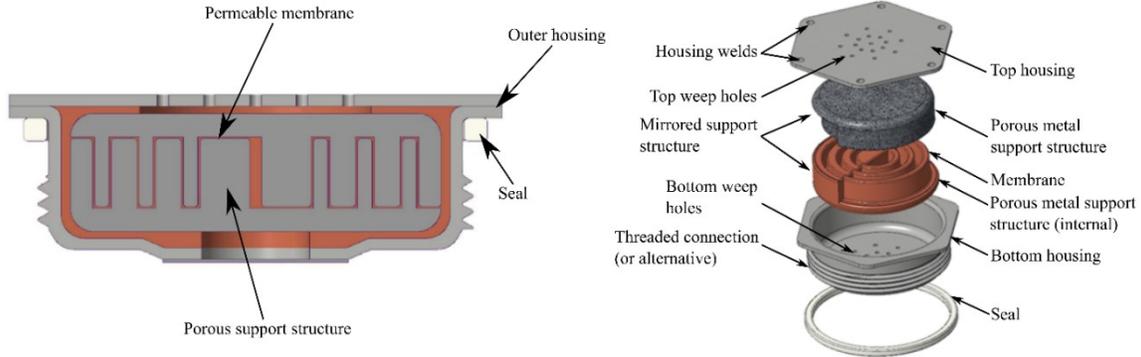


Figure 1: CAPS cross-section and exploded view of assembly.

$$\frac{dn_c}{dt} = \frac{dn_g}{dt} - \frac{dn_p}{dt} \quad (1)$$

where n_c is the number of moles collected in the control volume, n_g is the number of moles generated, and n_p is the number of moles permeated 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 here for the temperatures and pressures relative to the critical pressure and temperature of the gas. This is expressed as

$$PV = nRT \quad (2)$$

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 Kelvin. The molar gas generation rate, dn_g/dt can be derived from Eq. (2), assuming normal temperature and pressure (NTP) conditions as

$$\frac{dn_g}{dt} = \frac{P_{NTP}}{RT_{NTP}} \frac{dV_g}{dt} \quad (3)$$

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

$$\frac{dn_c}{dt} = \frac{V_{cv}}{RT} \frac{dP}{dt} \quad (4)$$

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.

Gas permeation is described by Fick's law [6]. This law requires intrinsic material properties, such as permeability, diffusivity, and solubility. Using Fick's law and the experimentally measured temperature dependent permeability, the H_2 permeation through a membrane is

$$\frac{dn_p}{dt} = \frac{A\phi}{h} P \quad (5)$$

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

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

which for simplicity can be put into the form

$$\frac{dP}{dt} + c_1 P = c_2 \quad (7)$$

where

$$c_1 = \frac{RT A\phi}{V_{cv} h} \quad (8)$$

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

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

$$M(t) = C e^{\int c_1 dt} \quad (10)$$

giving that

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

Note that as $t \rightarrow \infty$, Eq. (11) 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

$$Q(T) = AF(T) \quad (12)$$

where $Q(T)$ is the molar flow rate in mol/s and F is the permeation flux in mol/m²s. For the CAPS design presented in Section 2 the area A is controlled by the pattern imposed on the membrane. In this work it is modified by changing the number of periods in the square wave of the membrane.

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

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

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 i th species in a gas as

$$v_f = \frac{v_i}{v_{tot}} = \frac{p_i}{p_{tot}} \quad (14)$$

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. Assuming that the control volume contains only air and H_2 then the percent volume fraction $v_{f_{H_2}}$ for H_2 is

$$v_{f_{H_2}} = \frac{v_{H_2}}{v_a + v_{H_2}} \quad (15)$$

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

$$p_{H_2} = \frac{v_f}{1 - v_f} p_a \quad (16)$$

which can be used to calculate the H_2 partial pressure p_{H_2} as functions v_f and p_a .

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

$$P_2 = \frac{T_2}{T_1} P_1 \quad (17)$$

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

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

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

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

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 Fig. 1 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 [7]. Silicone permeability, which follows an Arrhenius relationship as a function of temperature, was calculated using the relationships

$$\begin{aligned}\phi_{40A}(T) &= 5.635 \cdot 10^{-8} e^{0.0193(T-273.15)} \\ \phi_{70A}(T) &= 3.467 \cdot 10^{-8} e^{0.0193(T-273.15)} \\ \phi_{26A}(T) &= \frac{\phi_{70A}(T) - \phi_{40A}(T)}{70 - 40} (26 - 40) + \phi_{40A}(T)\end{aligned}\quad (20)$$

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 2 shows a diagram of the test setup used to test the permeation rate of the prototype and Fig. 3 shows a picture of the physical hardware. The void volume for this test setup was approximately $2.43 \times 10^{-6} \text{ m}^3$. To perform the test CAPS was placed inside of a bell jar and both upstream and downstream was evacuated. A mass spectrometer was placed downstream of CAPS to measure the helium permeation. The spectrometer was calibrated using a helium leak standard downstream of CAPS. After it was calibrated a helium leak was released upstream and the amount of permeated helium downstream was measured as a function of time. Note that although the permeability was measured using H₂ and the test was performed using helium, the permeability of H₂ is approximately 1.5 times that of helium [8].

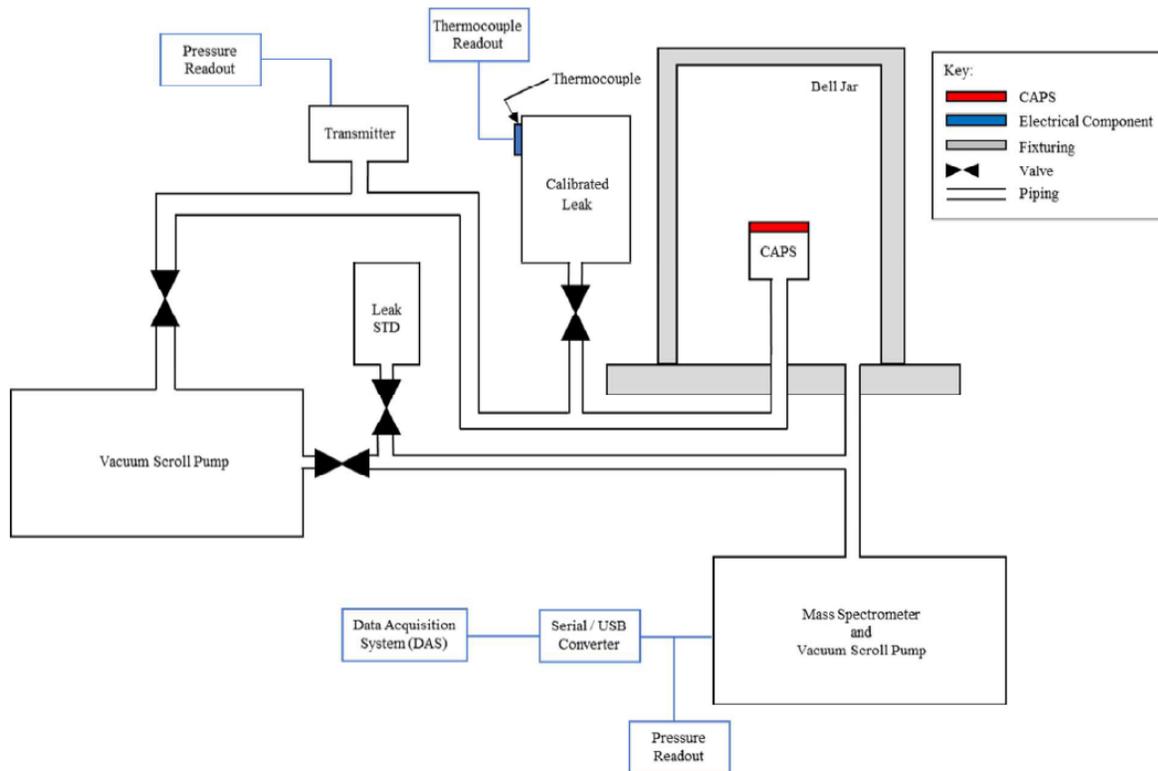


Figure 2: Diagram of experimental test setup for validating the analytical flow rate models.

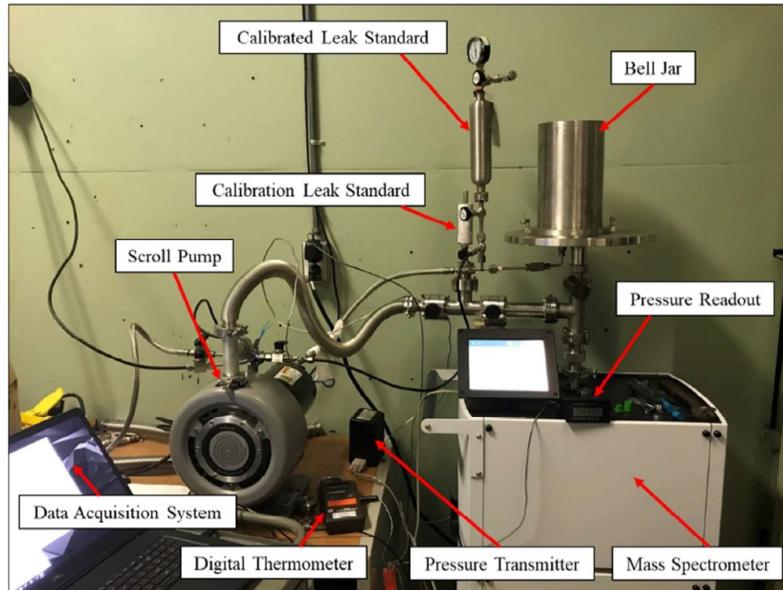


Figure 3: Experimental test set up for CAPS permeation testing.

Figure 4 shows a comparison of the analytical versus experimental flow rates. The closeness of these results verify that the analytical model accurately models the permeated gas through the membrane. Even though the 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. At this leakage rate, the steady-state volume fraction is approximately 0.6%.

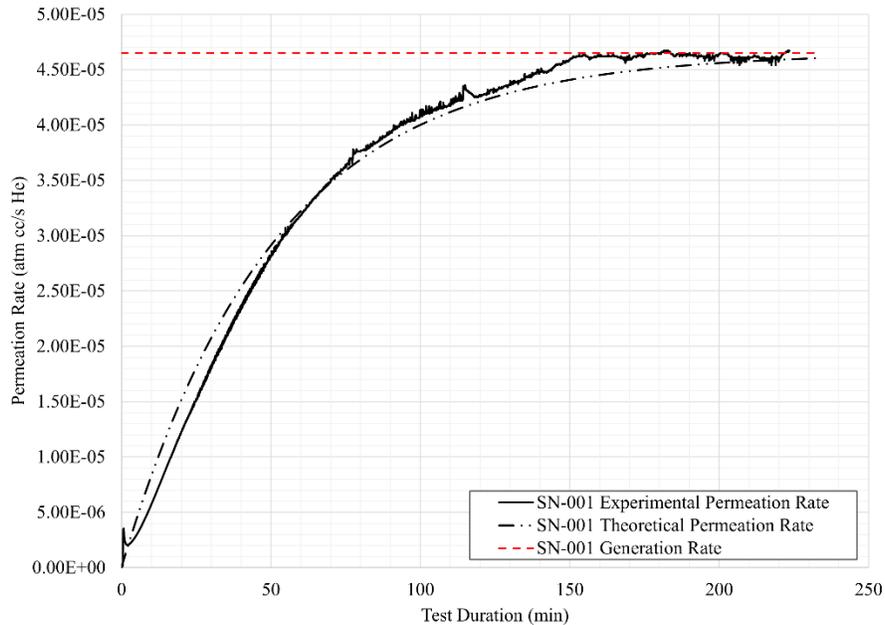


Figure 4: CAPS prototype experimental test results.

5. Example Application – 9979AF H₂ 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 because, for some approved contents, the H₂ generation mitigation requires sampling or purging after 180 days as well as limits on minimum void volume [9]. The use of CAPS could potentially allow for these restrictions to be removed.

Consider H₂ generation within a hypothetical 9979AF package, assuming H₂ generation is constant over time. The volumetric H₂ generation in cc/s is described by the equation

$$V = \frac{0.5DG(T)kv}{A_g} \quad (21)$$

where

$$G(T) = \begin{cases} G_{h_2o} & -40 \leq T \leq -15.6 \text{ }^\circ\text{C} \\ G_{hc}(T) & -15.6 < T \leq 67 \text{ }^\circ\text{C} \end{cases} \quad (22)$$

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

In Eqs. (21) – (23) $G_{hc}(T)$ represents the H₂ 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. (21) 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 9979AF package the bounding total decay heat is 11.8 mW [10].

Figure 5 shows the predicted H₂ permeation flow rate as a function of time, for $T_{stp} = 25 \text{ }^\circ\text{C}$, assuming the same void volume as the experimental setup. Note that the flow rate reaches the generation rate in approximately 25 minutes. At this temperature the H₂ gas takes up approximately 0.6% of the void volume, significantly lower than the 5% LFL.

As previously captured in Eq. (20) the silicone permeability is a function of temperature, following an exponential decay as temperature decreases. This suggests that the limiting flow rate for H₂ permeation will occur at low temperatures. Figure 6 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 H₂ 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.

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

	G_{h_2o}	D	k	ν	A_g	G_{T_1}	E_a	R_g	T_1	T
Unit/ 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 · mol	298.15 K	K

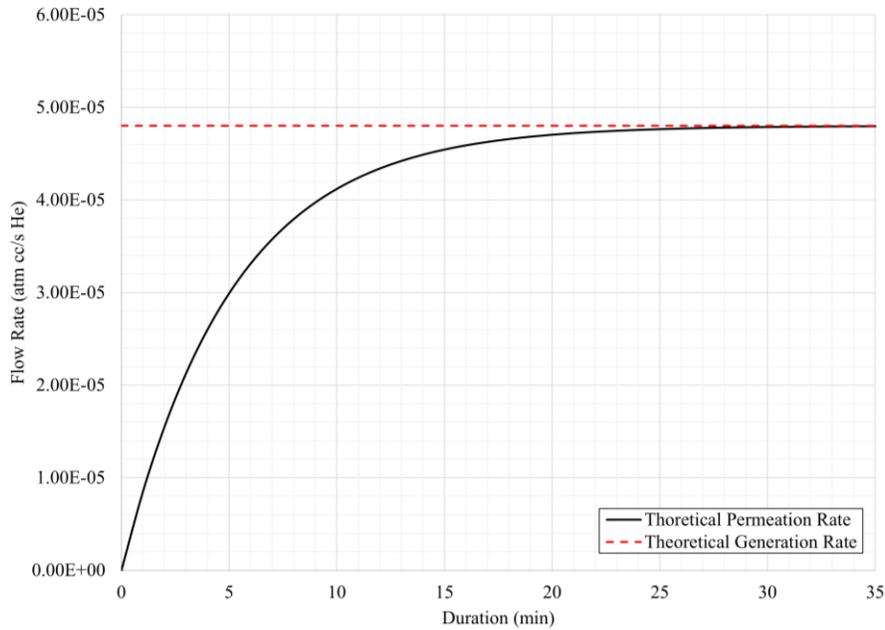


Figure 5: Theoretical permeation flow rate through CAPS on hypothetical 9979AF package.

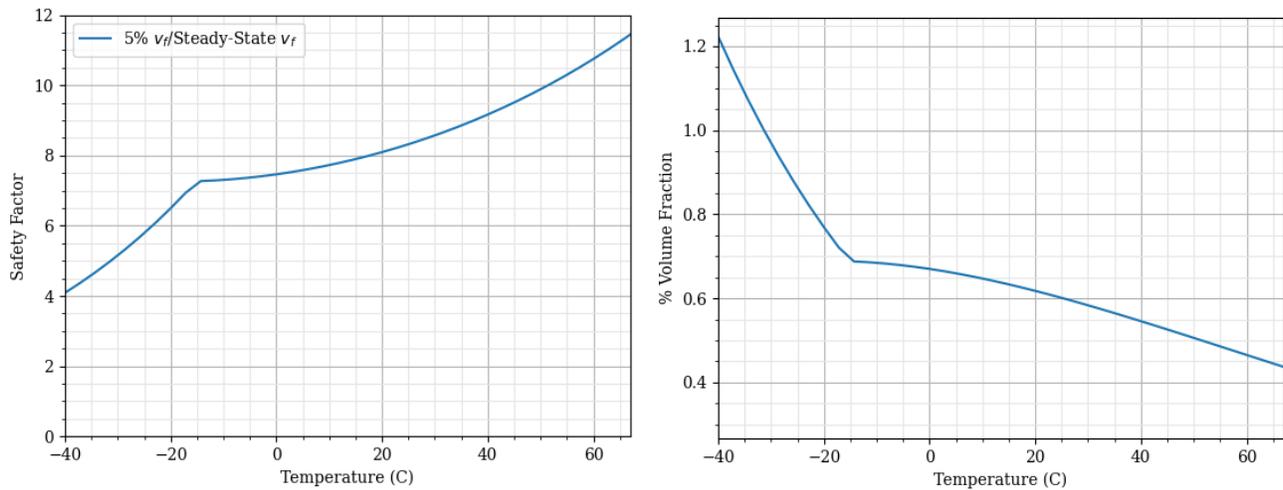


Figure 6: Safety factor and % volume fraction as a function of temperature, for steady state H_2 permeation out of a hypothetical 9979 package.

6. Conclusions

This work has presented a compact augmented permeation system designed to allow for the permeation of H₂ 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 H₂ 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 H₂ generation problems.

7. References

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