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Evaluation of SAES COMBOGETTER® for Use in Nuclear Material Transportation Packages

George M. Buffleben, Timothy J. Shepodd, Paul J. Nigrey

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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George M. Buffleben and Timothy J. Shepodd
Materials Chemistry Department
Sandia National Laboratories
Livermore, California 94550

and

Paul J. Nigrey
Engineering Sciences Research and Development Department
Sandia National laboratories
Albuquerque, NM 87185

Abstract

This report summarizes the testing of SAES COMBOGETTER® and evaluates its potential use as a hydrogen getter in nuclear material transportation packages. We measured the getters hydrogen uptake capacity, and uptake rates under different conditions including temperature, gas composition, and poisons. We also compared this getter to another commercially available hydrogen getter.

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Introduction

Materials referred to as getters, degassers, absorbers, or scavengers are being used to control gas in a variety of devices such as batteries, heat exhangers, vacuum tubes, glove boxes, and vacuum systems[1,2,3]. Because radiolysis of hydrogenous constituents of contact-handled (CH) transuranic (TRU) wastes may generate hydrogen gas (H_2), the U.S. Nuclear Regulatory Commission (NRC) has limited the amount of H_2 that may accumulate with CH-TRU wastes to 5 percent by volume, the flammability limit of H_2 in air. Identical limitations have been adopted by the U.S. Department of Energy (DOE) to certify transportation packaging within its purview. The use of hydrogen getters in transportation or storage packages thus represent a potential technological solution to preventing the buildup of undesirable gas that could represent safety hazards in such packaging. The use of getters in transportation packaging, however, thus far has been extremely limited.

The TRansUranic PACkage Transporter (TRUPACT-II) is an example of a transportation package that could use getters to control hydrogen pressure generation. In fact, the schematics for the TRUPACT-II show provisions for accommodating a getter (catalyst) in the upper and lower aluminum honeycomb spacer assemblies of the inner containment vessel[1]. Formal incorporation of getters within the TRUPACT-II is currently being proposed[1]. Since the Safety Analysis Reports[4] (SARs) of the TRUPACT-II have undergone a number of reviews by the Nuclear Regulatory Commission (NRC), it was important to attempt to ascertain the types of questions that the NRC would have concerning the use of getters in a package. While an attempt has been made in this report to address these issues in some fashion, each item will not be discussed specifically for a hydrogen getter at this time. The following list[1] shows the nature of the NRC's concerns regarding the use of getters in the TRUPACT-II or other Type B transportation packaging.

- *Capacity*: What is the getter's capacity relative to the potential total gas generated during one year?
- *Pressure*: What is the maximum normal operating pressure (MNOP) during one year? Is the getter's performance affected by pressure?
- *Poisons*: Are there any chemical constituents in the contents that could poison the getter?
- *Reversibility*: Under what conditions will the getter release hydrogen, and could these conditions occur during transport?
- *Temperature*: What is the effective temperature range of the getter relative to the temperature conditions specified in the Code of Federal Regulations[1] (-20°F to 100°F plus solar insulation)?
- *Humidity*: What is the effect of water vapor on the getter? Will frozen getter still work?
- *Location*: Does the location of the getter matter? Consider stratification of the gases.
- *Thermal*: Does the getter release/absorb heat? If so, is this factored into the thermal and structural analysis?

This report discusses the results of preliminary gas uptake tests performed at Sandia National Laboratories. These tests addressed the effects of poisons, temperature, gas mixtures, and humidity on the capacity and uptake rate of SAES COMBOGETTER®. This getter is designed to absorb atmospheric gasses, and hydrogen for maintaining a vacuum in vacuum insulated panels[1]. We conducted preliminary tests designed to evaluate the potential for using this as a hydrogen getter in nuclear material transportation packages. **It is understood that this application is different from the original design range of this getter and that results of this report have no bearing on COMBOGETTER® performance under conditions it was designed for.** Testing was started by measuring the getter's hydrogen uptake capacity. This was followed by a series of tests designed to measure hydrogen uptake rates under different conditions including exposure to temperatures of 20 °C and 100 °C, exposure to mixtures of hydrogen in several gasses, including water vapor, and potential poisons like carbon monoxide, and hydrogen fluoride. Finally, we tested another commercially available hydrogen getter.

Experimental

These experiments use explosive gas mixtures. No one should attempt to conduct such tests unless they are qualified and experienced explosive handlers, have well established safety procedures in place, and are prepared to safely contain any inadvertent detonation.

The apparatus for testing the hydrogen uptake rates was designed and built at Sandia. A photograph is shown in Figure 1, and a simplified schematic in Figure 2. The apparatus uses a 1,000 torr Baratron® pressure head and a 10,000 torr Baratron® pressure head, both made by MKS Instruments, Inc. These pressure heads are calibrated annually by MKS Instruments, Inc. and the resulting calibrations are traceable to the National Institute of Standards and Technology. The pressure data was acquired with a LabView NB-MIO-16XL data acquisition card in a Macintosh II CI running LabView V3.1. The digital resolution of the NB-MIO-16XL is 16 bits. With the system taking a data point every 10 minutes, the maximum pumping rate sensitivity is 4.5×10^{-5} standard cubic centimeters per second (std. cc s^{-1}) for these experiments. The COMBOGETTER® was purchased from SAES (4175 Santa Fe Road San Luis Obispo, CA 93401), while the certified gas mixtures of 4.98% hydrogen in argon, 4.98% hydrogen in nitrogen, 2.16% hydrogen in air, 1.05% carbon monoxide in air, and 1% hydrogen fluoride in nitrogen were purchased from Matheson Tri-gas. Hydrogen fluoride was supplied by Scott Specialty Gas Inc., and 99.99999% pure hydrogen was produced with a Whatman hydrogen generator model 75-30. Experiments using different concentrations of these gasses where made by mixing the gasses in the apparatus.

The SAES COMBOGETTER® is a combination of hydrogen, oxygen, carbon monoxide, carbon dioxide, and water getters in a metal cup. It has a diameter of 1.1 inches, a height of 0.28 inches, and a mass of 7.50 ± 0.15 grams. Samples of the COMBOGETTER® were placed on a 304 stainless steel stand (mass 12.937g) inside the reactor (Figure 3). The reactor has a valve that can isolate it from the rest of the apparatus without disturbing the contents. This allows us to load the getter into the reactor in an argon glove box. For each test, a new sample was loaded into the reactor either in the glove box or in the laboratory where it was exposed to room air for five to ten minutes. The argon or air was then pumped off, which took five to ten minutes. The various volumes in the apparatus were filled with the different gasses required for a particular test. These gasses were then expanded into each other and allowed to mix before being exposed to the sample. The laboratory is maintained at 20 ± 1 °C, and the reactor is wrapped in heating tape for experiments at elevated temperatures. All temperature and pressure measurements are recorded by computer. For comparison, we also ran experiments using a commercial getter from Vacuum Energy Inc. (VEI). This getter powder was loaded into a 20ml scintillation vial and a tissue was taped over the vial to avoid powder dispersion. These were then tested like the COMBOGETTER® samples.

To evaluate the COMBOGETTER® for water vapor exposure, the reactor was also loaded with 8.522g of ice, pumped down, and the ice was allowed to melt. No other gases were used in this ice test since the getter was clearly reacting with the water vapor to generate pressure and it would not be possible to make any meaningful calculations from the pressure data. As a follow up to this test, we placed a COMBOGETTER® on a stand in a 400ml beaker with 20ml water. The beaker was covered with Parafilm and left to sit for 31 hours.

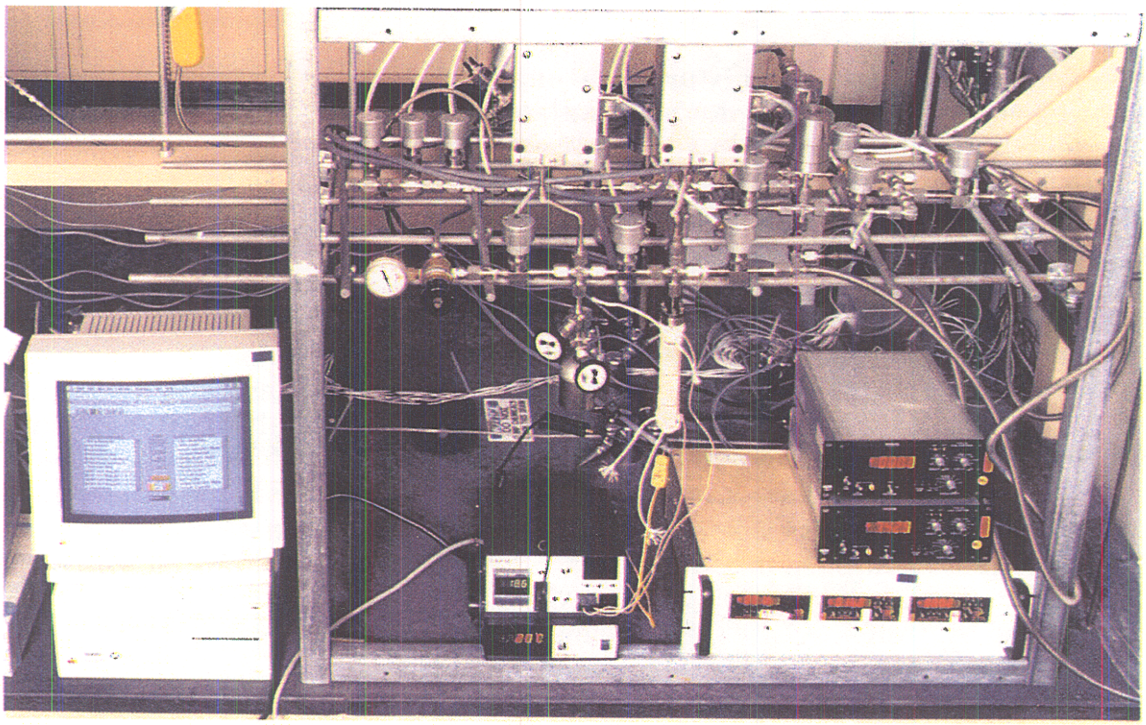

Figure 1: A photograph of the Sandia getter testing apparatus.

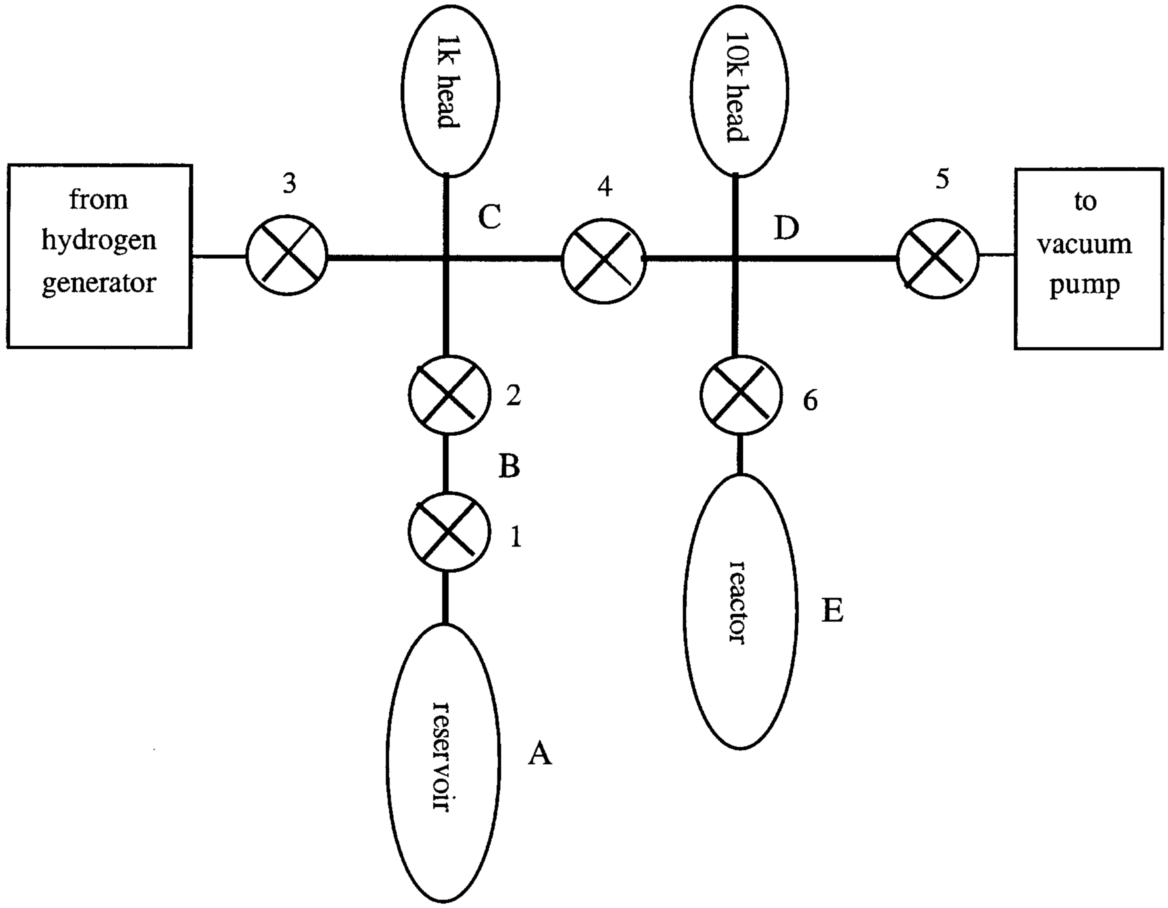

Figure 2: Schematic of apparatus. The volumes of the apparatus are as follows. The reactor volume has been corrected to account for the volume displaced by the sample and stand.

Volume A	102.5 ml
Volume B	3.9 ml
Volume C	15.2 ml
Volume D	28.1 ml
Volume E	88.7 ml

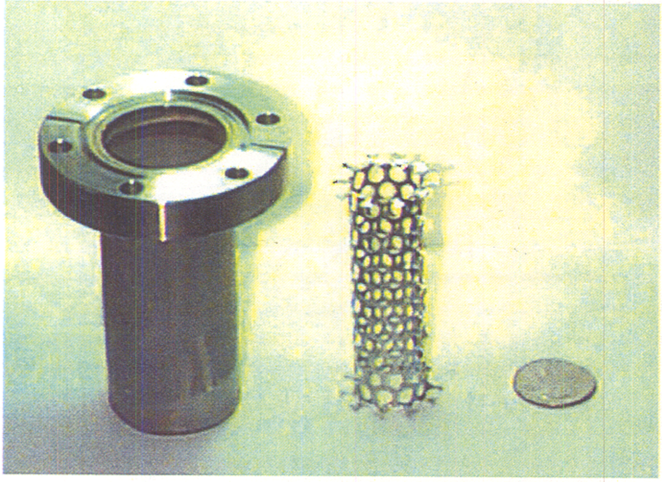 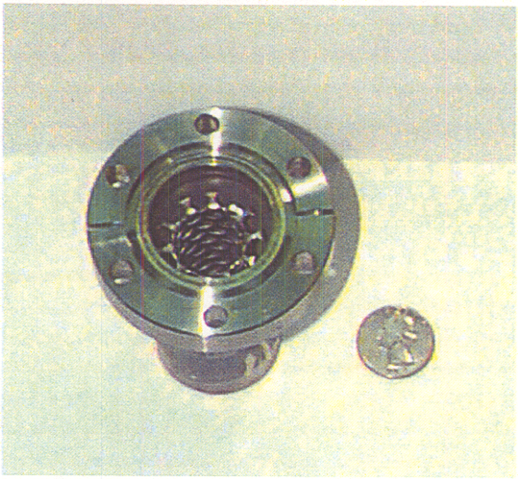

Figure 3: Photographs of the reactor and stand.

Results

The gas handling apparatus (Figures 1 and 2) has been used extensively by Sandia for testing numerous getters[1]. We have a high degree of confidence in the accuracy of the results obtained from this apparatus. Exact values of pumping speed can vary between experiments. Gas uptake rate is sensitive to pressure, temperature, other atmospheric constituents, hydraulic restrictions, physical placement of the getter, and degassing history. Pumping speeds should only be compared when generated in the exact same apparatus or when the differences caused by changing apparatuses are quantified. The authors highly recommend testing of any pumping speed under conditions most representative of the intended deployment.

The first four experiments were run in pure hydrogen to measure capacity and the hydrogen uptake rate. The first COMBOGETTER® was loaded into the reactor in an argon glove box, while the second was briefly exposed to laboratory air. Both were then degassed and given doses of hydrogen at 20 °C until uptake essentially stopped as indicated by the pressure-time plot. (Figure 5). These experiments were repeated with two more samples run at 100 °C, each given a single large dose of hydrogen (Figure 6). At both temperatures, the brief exposure to air caused a decrease in the getter uptake rate, and an increase in the getter capacity (Table 1). At 100 °C, the uptake rates increased significantly and the capacity showed an increase as well. These are best case rates since hydrogen uptake will always be limited by diffusion through air in transportation packages. The most important result of these four tests is a measurement of the hydrogen capacity. Considering that in a transportation package the getter will be exposed to air and that 20 °C is a reasonable expectation of the loading operations the getter is likely to see on a regular basis, one can expect a capacity of 250 standard cc hydrogen per getter disk. For comparison purposes we loaded the reactor with an equivalent mass (7.358 grams of formula 12-98c) of a commercial hydrogen getter from Vacuum Energy Inc. (VEI), and gave it a single large dose of hydrogen. Its uptake rate was 10 to 100 times greater than that of the COMBOGETTER®, and with a rated capacity of 100 standard cc hydrogen per gram, it can absorb three times as much hydrogen per gram.

Run conditions	Hydrogen capacity (std. cc H_2)	Initial uptake rate (std. cc H_2 s^{-1})
No air exposure, 20 °C, SAES getter	229.5	3.3×10^{-2}
Air exposure, 20 °C, SAES getter	248.6	2.6×10^{-2}
No air exposure, 100 °C, SAES getter	274.9	7.7×10^{-1}
Air exposure, 100 °C, SAES getter	283.9	1.9×10^{-1}
Air exposure, 20 °C, VEI getter	100 g^{-1}(rated)	1.2

Table 1: Hydrogen capacities and initial uptake rates for getters exposed to hydrogen only. Hydrogen capacity VEI getter is rated at 100 std. cc H_2 per gram getter, all other values are giving per sample tested.

In the next series of tests, the COMBOGETTER® was exposed to 5.0% hydrogen in argon, 5.0% hydrogen in nitrogen, and 5.7% hydrogen in air. These test were run at 20 °C (Figure 7) and then repeated with the reactor heated to 100 °C (Figure 8) to get a measure of how the getter would perform in different atmospheres and temperatures. As expected, the gross uptake rates dropped due to the diffusion of hydrogen through the bulk gas to the hydrogen depleted volume around the getter. However, this condition approximates the hydrogen uptake rates that can be expected in the transportation packages.

Gas mixture	Initial uptake rate (std. cc gas s^{-1})
5.0% hydrogen in argon at 20 °C	3.2×10^{-3}
5.0% hydrogen in nitrogen at 20 °C	2.4×10^{-3}
5.7% hydrogen in air at 20 °C	5.1×10^{-3}

Table 2: Bulk uptake rates for SAES getter exposed to 5% hydrogen in gas.

The COMBOGETTER® is designed to absorb most atmospheric gasses, but it does not absorb argon. Therefore, it is important to look at the test results of 5.0% hydrogen in argon to see that the hydrogen is being removed and not just other atmospheric gasses. This is most clearly seen in table 3 were the hydrogen is removed from hydrogen in argon, but some of the bulk gas is absorbed in the tests containing air and nitrogen giving a larger total amount of gas absorbed. It then becomes important to look at the test results from 5.7% hydrogen in air to see that it can be done safely. By looking at the uptake of gas in these tests, we see that this getter can safely remove the danger from an explosive mixture of hydrogen in air. No detonations or ignition event occurred in any of our tests.

Gas mixture	Gas absorbed (net moles decreased)
5.0% H_2 in Ar at 20 °C	5.0%
5.0% H_2 in N_2 at 20 °C	9.9%
5.7% H_2 in air at 20 °C	8.6%
5.0% H_2 in Ar at 100 °C	4.7%
5.0% H_2 in N_2 at 100 °C	9.9%
5.7% H_2 in air at 100 °C	9.7%

Table 3: Gas absorbed by getter when exposed to 5% hydrogen/gas mixture.

In the final series of tests, we looked at how carbon monoxide, hydrogen fluoride, and water vapor impact the performance of the getter. These gases can be found in transportation packages containing nuclear material and could effect getter performance[1]. The carbon monoxide had a little effect on the getter and hydrogen fluoride had a larger but still not significant effect on getter performance (Figure 9).

Gas mixture	Initial uptake rate (std. cc gas s^{-1})	Gas absorbed (net moles decreased)
5.7% H_2 in air at 20 °C	5.1×10^{-3}	8.6%
0.99% CO/ 6.0% H_2 in air at 20 °C	5.4×10^{-3}	10%
0.91% HF/ 6.1% H_2 in N_2 at 20 °C	1.9×10^{-3}	7.7%
0.99% HF/ 5.9% H_2 in air at 20 °C	7.1×10^{-3}	10%

Table 4: Initial uptake rates and percent of gas absorbed when getter is exposed to poisons. Hydrogen in air is listed for comparison.

To maintain a moist environment for testing the getter in water vapor, we loaded 8.5 grams of ice into the reactor, pumped out the air, and let the ice melt. After several hours, the pressure increased to 359 torr, well above the 18 torr for the vapor pressure of water. This suggests that the getter is reacting with the water to generate hydrogen at a rate greater than the getter can absorb. While exposed to the water vapor, the getter increased in mass by 0.539g and swelled substantially causing deformation, cracking, and flaking. This test was repeated in air by placing a fresh getter disk over 20ml of water in a covered beaker. Over the next day the getter swelled, cracked, flaked, and increased in mass by 0.697g (figure 4). The COMBOGETTER® is a water getter and should not be used where it is exposed to amounts of water greater than its capacity.

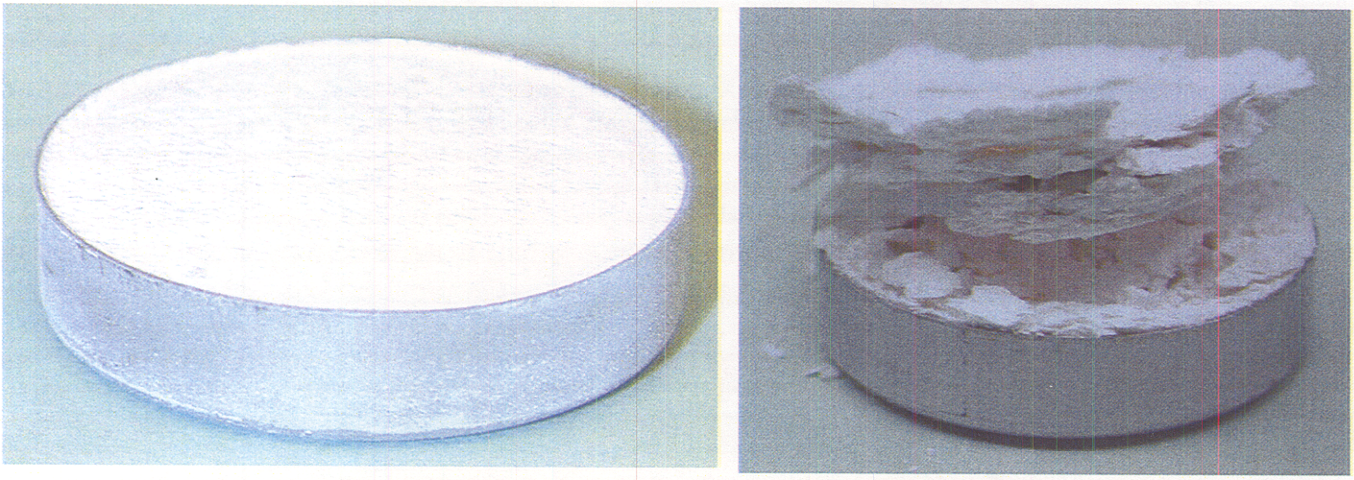

Figure 4: Photographs of new getter and after 31-hour exposure to moist air.

Conclusions

In many ways, the SAES COMBOGETTER® performed well in these tests. It took up hydrogen at a variety of pressures. In pure hydrogen, it absorbed gas from pressures of 300 to 1325 torr. This is a range of pressures far greater than what one would see in transportation packages. The amount of hydrogen absorbed varied a bit depending on run the conditions, and the uptake rate increased substantially with increased temperature. Considering that the getter will be exposed to air at 20 °C during loading operations, one can expect a capacity of 250 standard cc hydrogen per getter disk. In all cases tested, the getter took up more than 200 standard cc hydrogen. The COMBOGETTER® successfully demonstrated that it could safely remove the explosive hazard of hydrogen in air by taking up the hydrogen without igniting it. When tested in the presents of carbon monoxide and hydrogen fluoride, ether of which could have potentially poisoned the getter, it performed well. These gasses had a small effect on uptake rates and capacity. When exposed to water vapor, the getter performed poorly. Even though the COMBOGETTER® is designed to absorb water vapor, it has a limited a capacity. The COMBOGETTER® is not designed to perform in environments beyond its water capacity. This capacity is easily exceeded in a humid environment, at which point the COMBOGETTER® appears to react with the water. This reaction may be hydrogen generation. If hydrogen is truly being generated by the getter in the presents of water this would only exacerbate the dangerous buildup of hydrogen in this application. The water vapor also caused the getter to swell, which caused cracking and flaking. The recently invented VEI getter merits further evaluation as it has a capacity of 100 standard cc hydrogen per gram and an uptake rate 10 to 100 times the COMBOGETTER®. The VEI getter is unaffected by water vapor or ice[1]. When considering the performance of the COMBOGETTER® in water vapor we can not recommend it for use in nuclear material transportation packages unless exposure to water can be minimized.

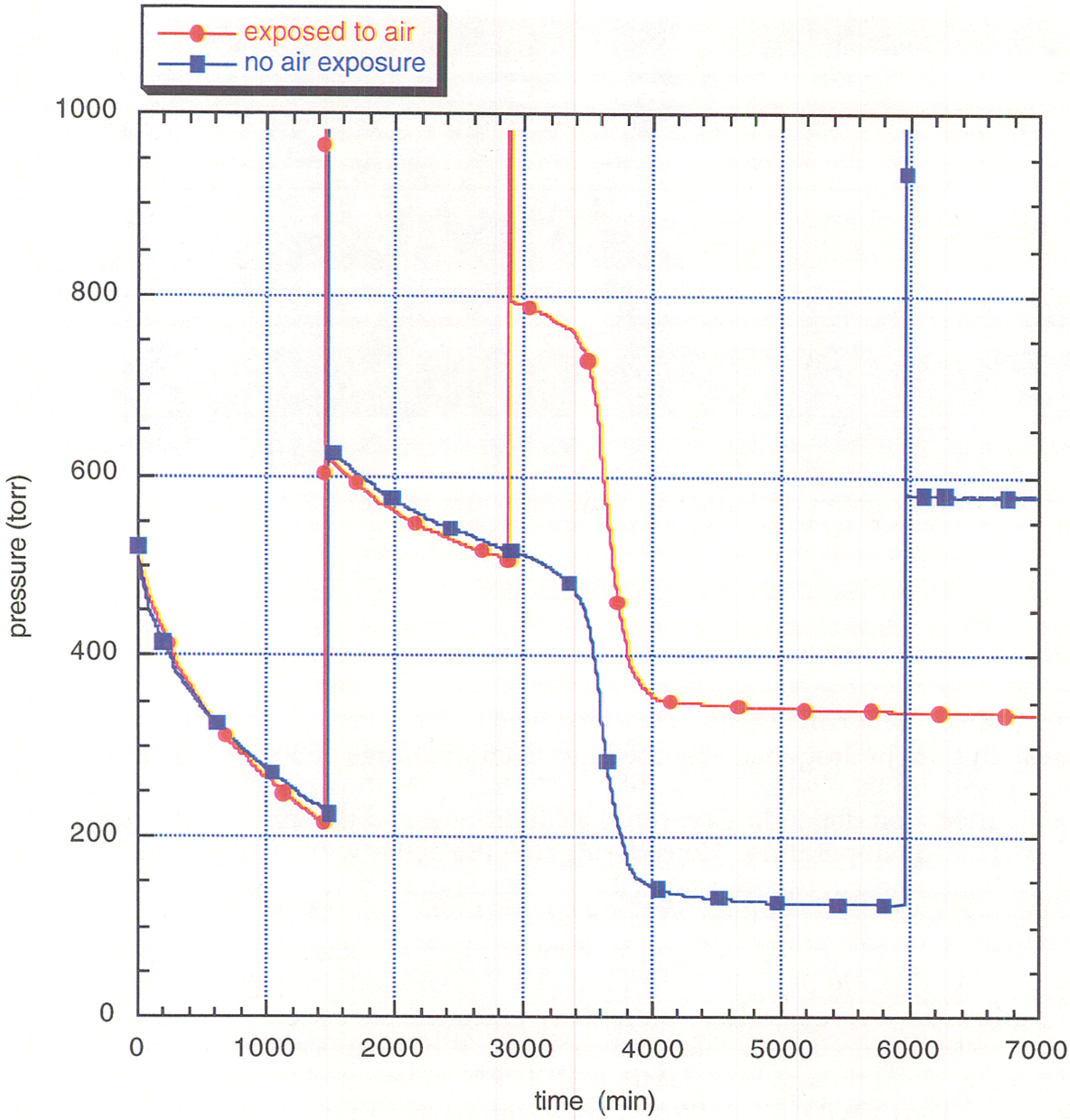

Figure 5: A comparison of hydrogen uptake by the COMBOGETTER® when exposed to air with one not exposed to air. Samples were run in hydrogen only at 20 °C, and given multiple doses of hydrogen.

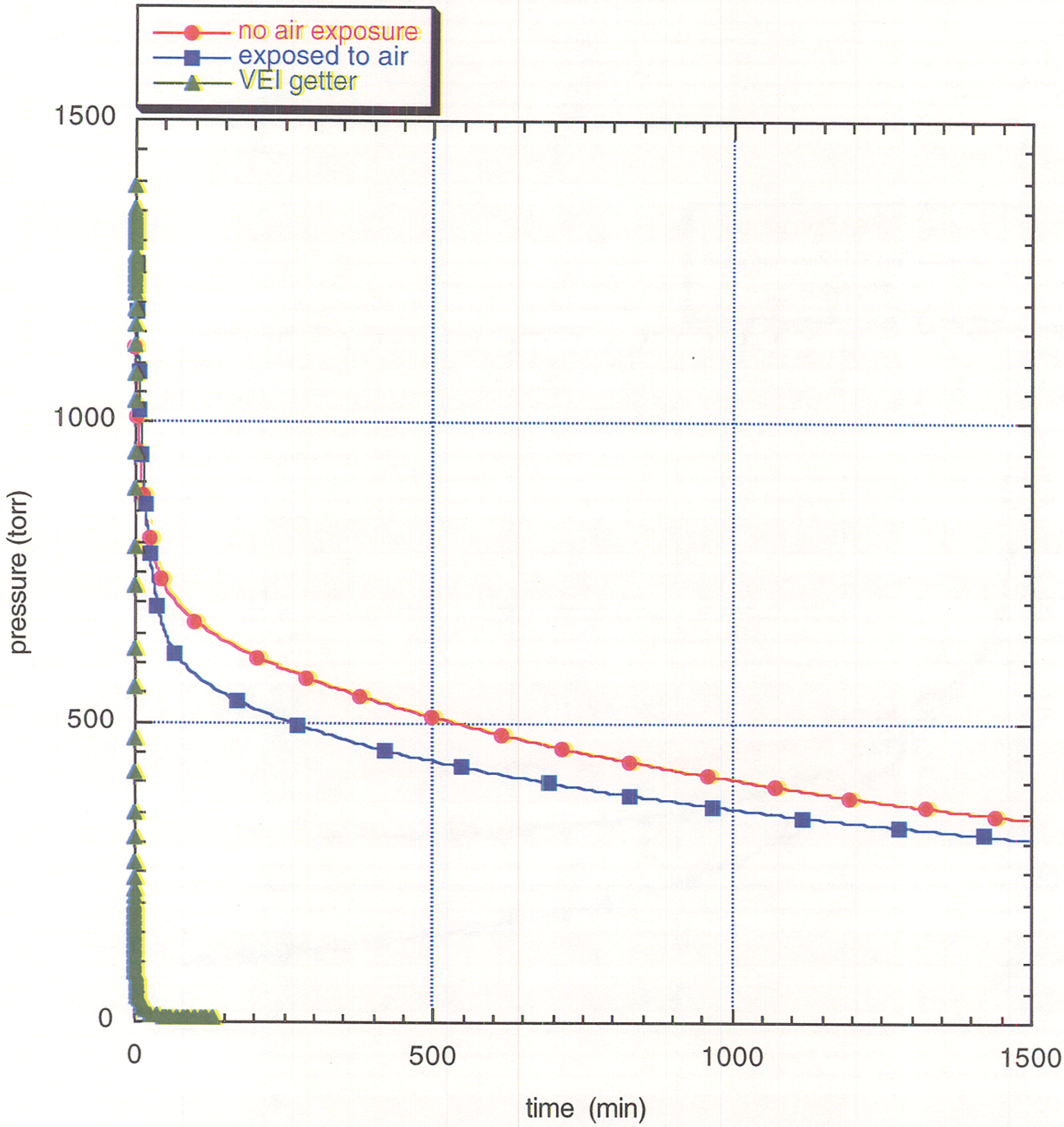

Figure 6: A comparison of the COMBOGETTER® exposed to air with one not exposed to air, and VEI getter. Both COMBOGETTER® samples were run at 100 °C, while the VEI getter was run at 20 °C. All three samples were given a single dose of hydrogen.

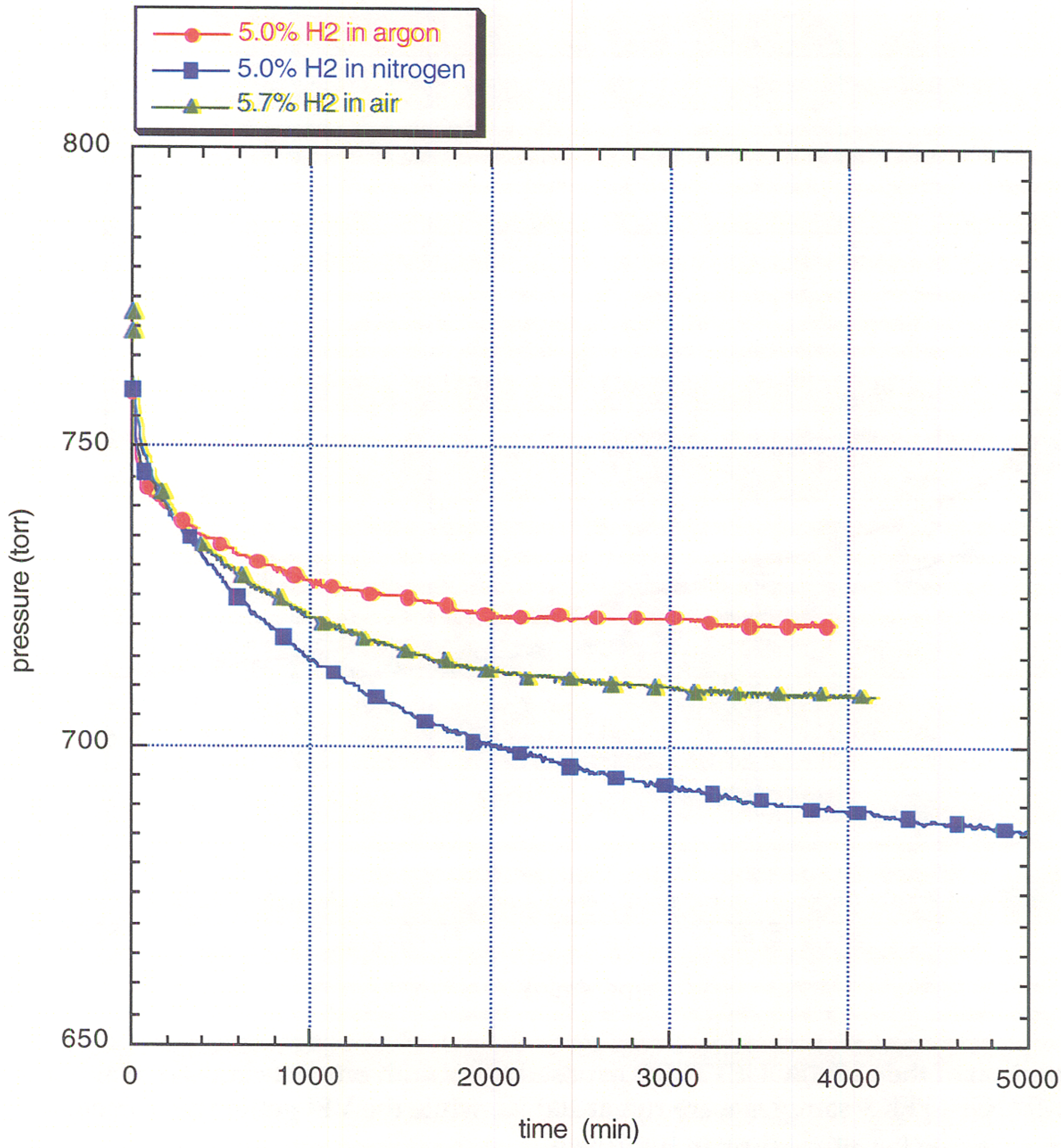

Figure 7: A comparison of gas uptake by the COMBOGETTER® when exposed to 5% hydrogen in different gasses at 20 °C

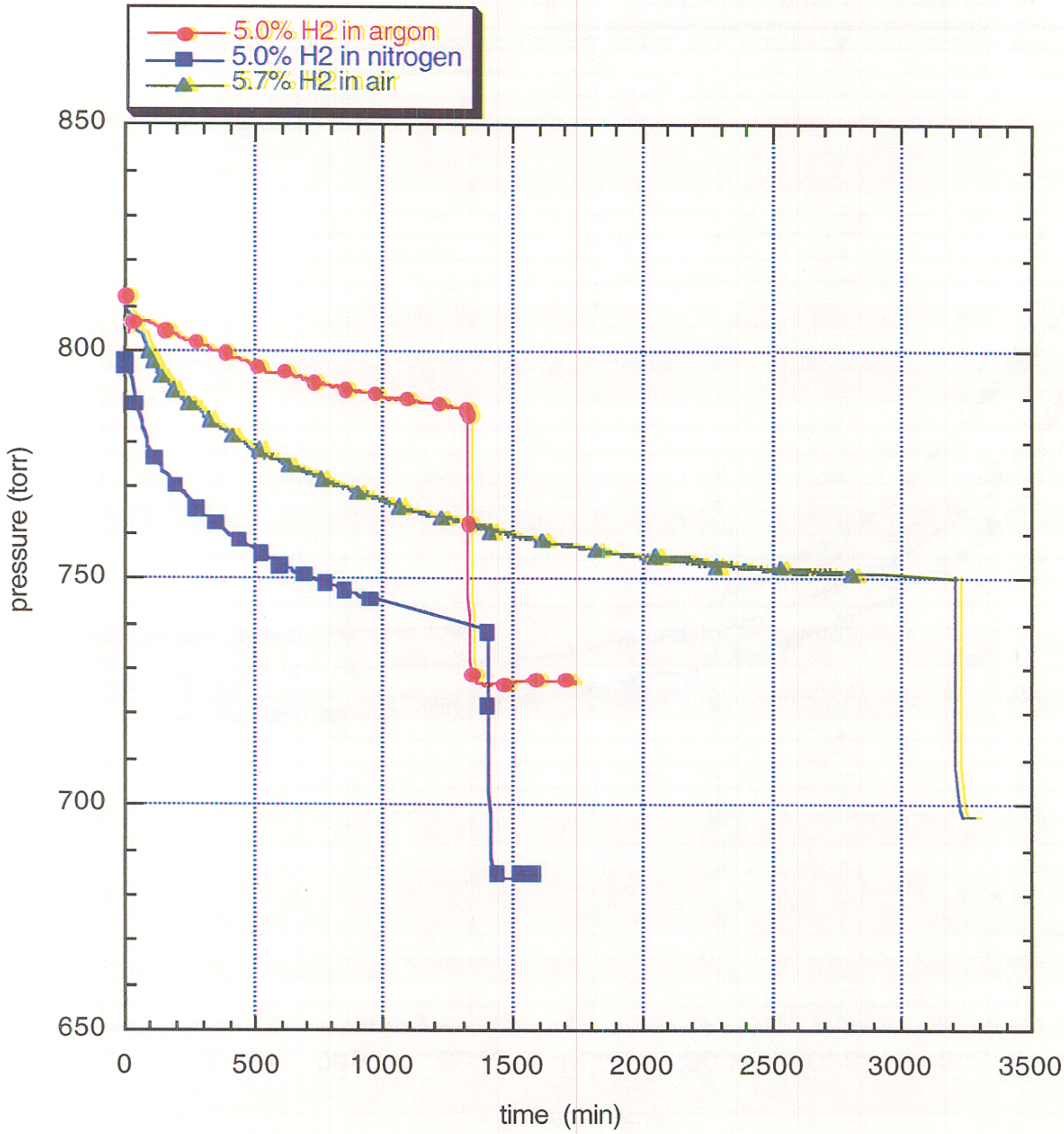

Figure 8: A comparison of gas uptake by the COMBOGETTER® when exposed to 5% hydrogen in different gasses at 100 °C. The pressure drop at the end of each trace is do to the reactor being cooled to room temperature.

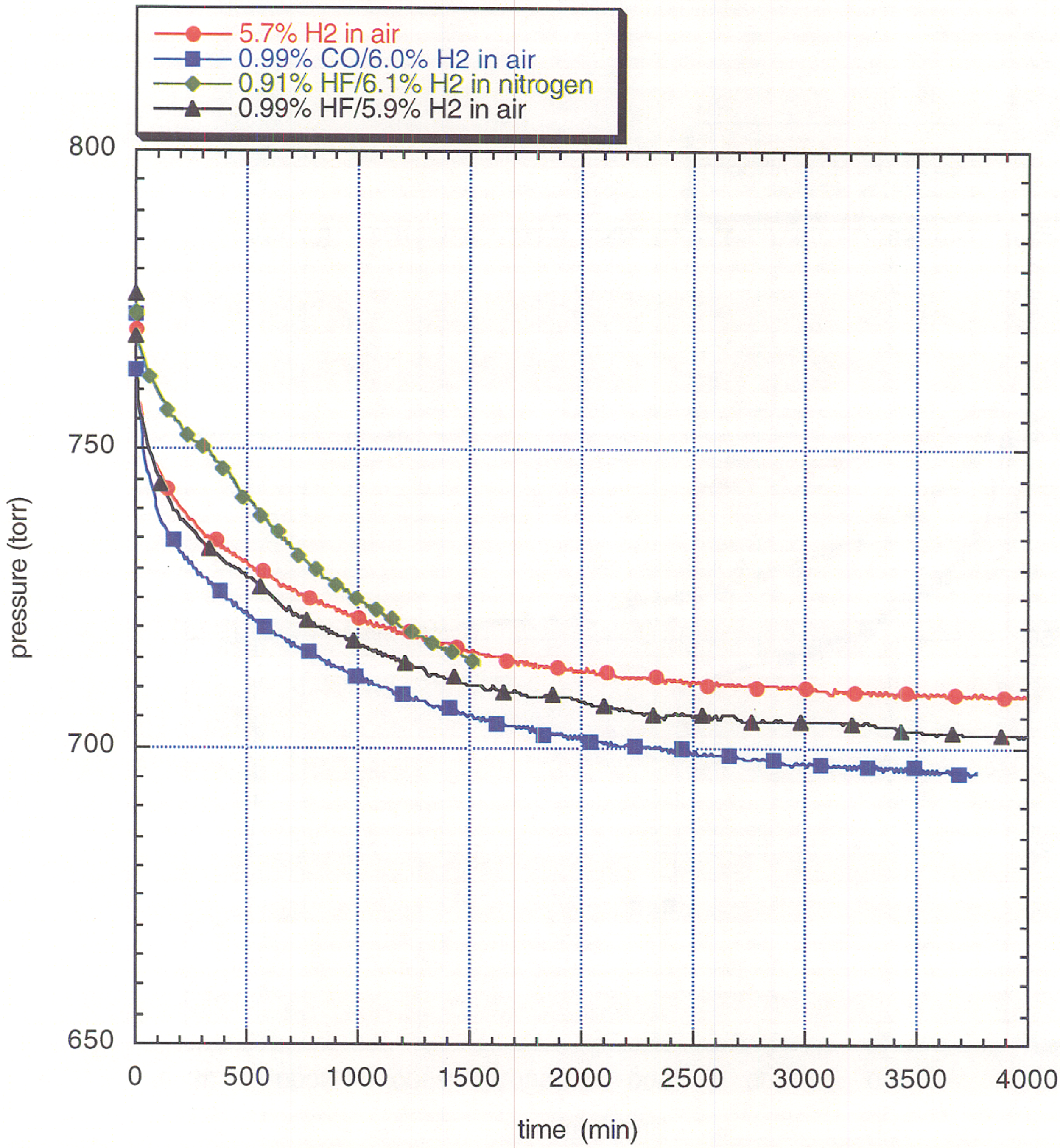

Figure 9: A comparison of gas uptake by the COMBOGETTER® when exposed to different poisons at 20 °C.

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