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The Effects of Temperature and Carbon Tetrachloride on Polymer Based Hydrogen Getters

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Abstract

This report summarizes hydrogen pumping by organic getters in the presence of carbon tetrachloride, and how the reduction of pumping in the presence of this catalyst poison can be minimized through the choice of catalyst. Catalyst A is shown to be preferred in a clean environment, and catalyst B for a poisoned environment. Additional, we examine the effects of temperature on pumping rates, and show that this getter is effective over a large temperature range from –23 to 107 degrees Celsius.

The Effects of Temperature and Carbon Tetrachloride on Polymer Based Hydrogen Getters

Introduction

Polymer based getters were invented at Sandia National Laboratories and are produced commercially for consumer and industrial products where hydrogen accumulation is a safety concern. This report discusses the results of hydrogen gas removal (pumping) tests performed at Sandia National Laboratories. These tests were conducted to see how organic getters would perform in the presence of a gas that would poison the getters' catalyst. The tests were conducted with two hydrogen getters that differed only in the catalyst composition (A or B). The getters were forced to compete with each other for a limited amount of hydrogen to determine which catalyst performed better when exposed to different gas mixtures. We also examined the effects of temperature on pumping rates, using getter made with catalyst A.

Experiments

The gas handling apparatus (Figure 1) has been used extensively by Sandia for evaluation of numerous getters. We have a high degree of confidence in the accuracy of the results obtained from this apparatus. However, since the stainless steel apparatus is opened to the air on a daily basis, high vacuum measurements are limited by our ability to degas the reactor of absorbed atmospheric species. As a practical matter, vacuum levels ≤ 0.01 torr require that extra attention be paid to the degas cycle. We are unable to bake out the entire apparatus, so we typically operate with a few millitorr of residual gas during long experiments with sealed volumes. The apparatus includes both a 1000 torr and 10 torr MKS pressure heads manufactured by Baratron. Data is 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 logging a data point at least every 10 minutes, we have a maximum pumping rate sensitivity of 1.5×10^{-7} std. cc s^{-1}.

Testing was done on two getters that differed only in the catalyst used (A or B). A 1.00 gram sample of getter power was loaded into a test tube. A Kimwipe was taped over the opening of the test tube to avoid powder dispersion. The getter samples were degassed at 100 °C for at least 2 hours 10 minutes, as recommended by Vacuum Energy, Inc., before being dosed with the appropriate gas.

To better compare the two getters a second set of experiments was conducted in which the getters were allowed to compete for available hydrogen in the apparatus. Four polypropylene containers (two of each getter) were loaded with 75 to 85 mg of getter each. A Kimwipe was then taped over each container to avoid powder dispersion. The four containers were taped together and loaded into the reactor. Getter masses were matched within a given experiment. The samples were sealed in the reactor and degassed at 100 °C for 2 hours 10 minutes. They were then exposed to hydrogen, or diluted hydrogen, with pressure changes recorded by the computer.

NMR was used to determine how much hydrogen each sample absorbed. NMR samples were prepared by mixing excess quantity of chloroform-d with the getter to dissolve the organic component, and then filtering through magnesium sulfate and a 0.45 μm PTFE filter to dry the sample and remove particles. A Varian Gemini 300 MHz NMR was used to acquire a proton spectrum. The relative integrals of the single and double bond regions were used to calculate the hydrogen uptake of the getters. Hydrogen pumping rates were calculated from the pressure change data, and are average rates for the pressure drop from 90 to 25 torr.

For hydrogen pumping rates at different temperatures, a 1.02 gram power sample of catalyst A getter was loaded into a test tube and a Kimwipe was taped over the opening. The sample was loaded into a reactor and degassed at 100 °C for 2 hours 10 minutes. Volume A (Figure 2) was filled with ≈ 19 torr of hydrogen. Volumes A and E were chilled to –23 °C using an o-xylene/liquid nitrogen bath. The hydrogen was then exposed to the sample, and pressure changes were recorded by the computer. This experiment was repeated four more times using the same getter sample and pumping off any remaining gas between experiments. The second run was done with an ice water bath, and for the last two runs volume E was wrapped in heating tape. Hydrogen pumping rates were calculated from the pressure change data, and are average rates for the pressure drop from 10 to 7 torr.

Argon was purchased from Matheson Tri-gas, while 99.99999% pure hydrogen was produced with a Whatman hydrogen generator model 75-30, and carbon tetrachloride was purchased from Aldrich. Experiments using different concentrations of these gasses where made by mixing the gasses in the apparatus and are reported as mole percent.

Results

We are interested in how the polymer base getters perform when exposed to a gas that poisons the catalyst and how different catalysts effect getter performance. We made two getters that were identical except for the catalyst used (A or B). We chose carbon tetrachloride as the poison because chlorinated hydrocarbons are known to be strong

poisons for these getters. The greater the chlorine content in the poison molecule, the greater the effect on the getter catalyst. Initial tests on each getter were done with a surplus of pure hydrogen. However, the results were difficult to compare since the hydrogen pumping rates were limited only by diffusion through the getter, and were nearly equal. To gain a better understanding of how the choice of catalyst affects the performance of the getters, we set up a competition between them in which both getters were placed into the same reactor and given a dose of hydrogen which was much less than theoretical capacity. The amount of hydrogen absorbed by each getter was quantified by ^{1}H NMR. In the next two tests, the samples were dosed with 10% and 20% of the getters' theoretical capacity using pure hydrogen. The A getter outperformed the B getter by adsorbing 3.4 and 2.6 times as much hydrogen, respectively.

In the next series of four tests the samples were exposed to a gas mixture containing argon or carbon tetrachloride mixed with hydrogen equal to 20% of the getters capacity. Argon was chosen as an inert control gas and slows the absolute pumping rate as a diluent, but does not change the relative reaction rates (Table 1). The carbon tetrachloride made a significant difference in the performance of the getters. With an atmosphere containing only 0.17% CCl_4, the A getter removed 1.5 times as much hydrogen as the B getter, and with 14.7% CCl_4, the A getter pumping dropped to 0.21 times as much hydrogen as the B getter. This clearly shows that while getter made with catalyst A will generally perform better under normal circumstances, in a poisoned environment getter B would be a superior choice.

Gas Composition	Ratio of hydrogen removed (A:B)
H_2 (10% getters' capacity)	3.4
H_2	2.6
0.15% Ar in H_2	2.5
14.7% Ar in H_2	2.4
0.17% CCl_4 in H_2	1.5
14.7% CCl_4 in H_2	0.21

Table 1: Ratio of hydrogen removed by getter A to hydrogen removed by getter B. Amount of hydrogen used is 20% of getters' capacity unless stated otherwise.

One should also look at the hydrogen pumping rates during these tests (Figure 3). In comparing the rates for hydrogen uptake in hydrogen/argon mixtures one can see a drop in the rate (Table 2) as expected due to diffusion of hydrogen through argon. A greater drop in rate can be seen in the samples exposed to carbon tetrachloride due to poisoning of the catalyst as well as diffusion of hydrogen through carbon tetrachloride. Finally, it should be noted that the pressure in experiments with carbon tetrachloride drops below the theoretical pressure predicted for the amount of carbon tetrachloride in the apparatus. This indicates that some of the carbon tetrachloride is absorbed by the getter.

Gas Composition	Hydrogen removal rate (std cc H_2 s^{-1} g^{-1})
H_2	1.1×10^{-2}
0.15% Ar in H_2	9.0×10^{-3}
14.7% Ar in H_2	5.7×10^{-3}
0.15% CCl_4 in H_2	6.2×10^{-3}
14.7% CCl_4 in H_2	2.2×10^{-4}

Table 2: Hydrogen removal rates for getters exposed to gas mixtures. Rates are averages from 90 to 25 torr.

In a second set of experiments we looked at the performance of getter A at different temperatures (Figure 4). A 1.02 gram sample was placed into the reactor and degassed at 100 °C for 2 hours 10 minutes. The reactor was cooled or heated to the desired temperature, and the sample exposed to a small amount of hydrogen. The same sample was used in this series of tests and any remaining gas was pumped off between each test. The capacity of the getter used in each test was so small (≈2%) that the rate was essentially unaffected by the reduction in capacity. The lowest temperature had the slowest adsorption rate, and the rate increased with temperature, as expected.

Temperature (°C)	Hydrogen removal rate (std cc H_2 s^{-1} g^{-1})
-23	2.4×10^{-4}
1	1.5×10^{-3}
19	6.5×10^{-3}
70	5.0×10^{-2}
107	6.8×10^{-2}

Table 3: Average hydrogen removal rate for getter A from 90 to 25 torr.

Exact values of pumping rates 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 rates 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 pumping rates under conditions representative of the actual deployment.

Conclusion

Chlorinated hydrocarbons poison the getter, but do not stop hydrogen pumping completely. The getter still removes hydrogen at a reduced rate even when the poison concentration is as high as 14.7%. The effect of carbon tetrachloride can be minimized through appropriate choice of a catalyst. Catalyst A is best suited for getters not expected to see any poisons; catalyst B should be used for getters in poisoned environments. A mix of the two catalysts may make for a good general getter with a broader range of operating environments.

Pumping rates for getter A were measured at different temperatures. The getter performs well over a large temperature range (-23 to 107 °C), although over this temperature range the pumping rate changes by more than two orders of magnitude. The getters' performance in a particular application will depend on a number of factors including hydrogen generation rate, amount of getter, temperature, poisons, and hydrogen diffusion through other gases.

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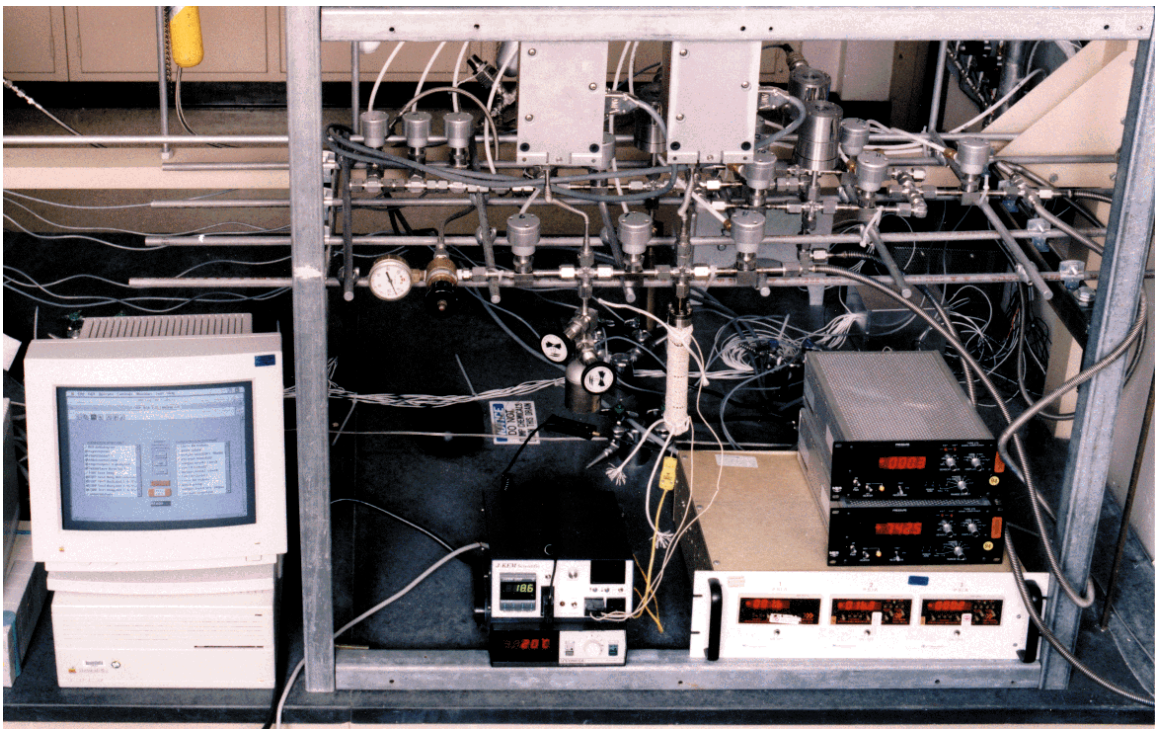

Figure 1. A photograph of the Sandia getter testing apparatus.

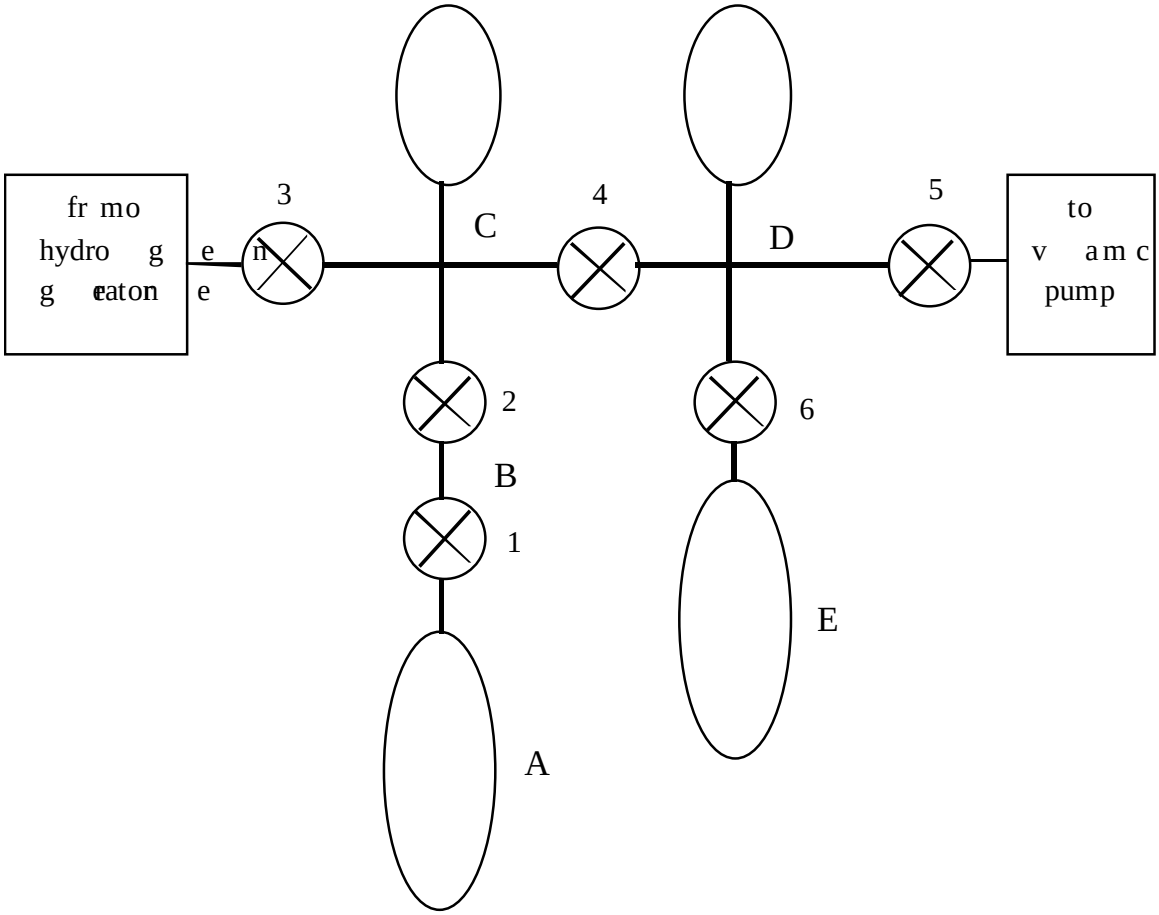

Figure 2. Schematic of apparatus. The volumes of the apparatus are as follows.

A	102.5 ml
B	3.9 ml
C	15.2 ml
D	18.5 ml
E	39.0 ml

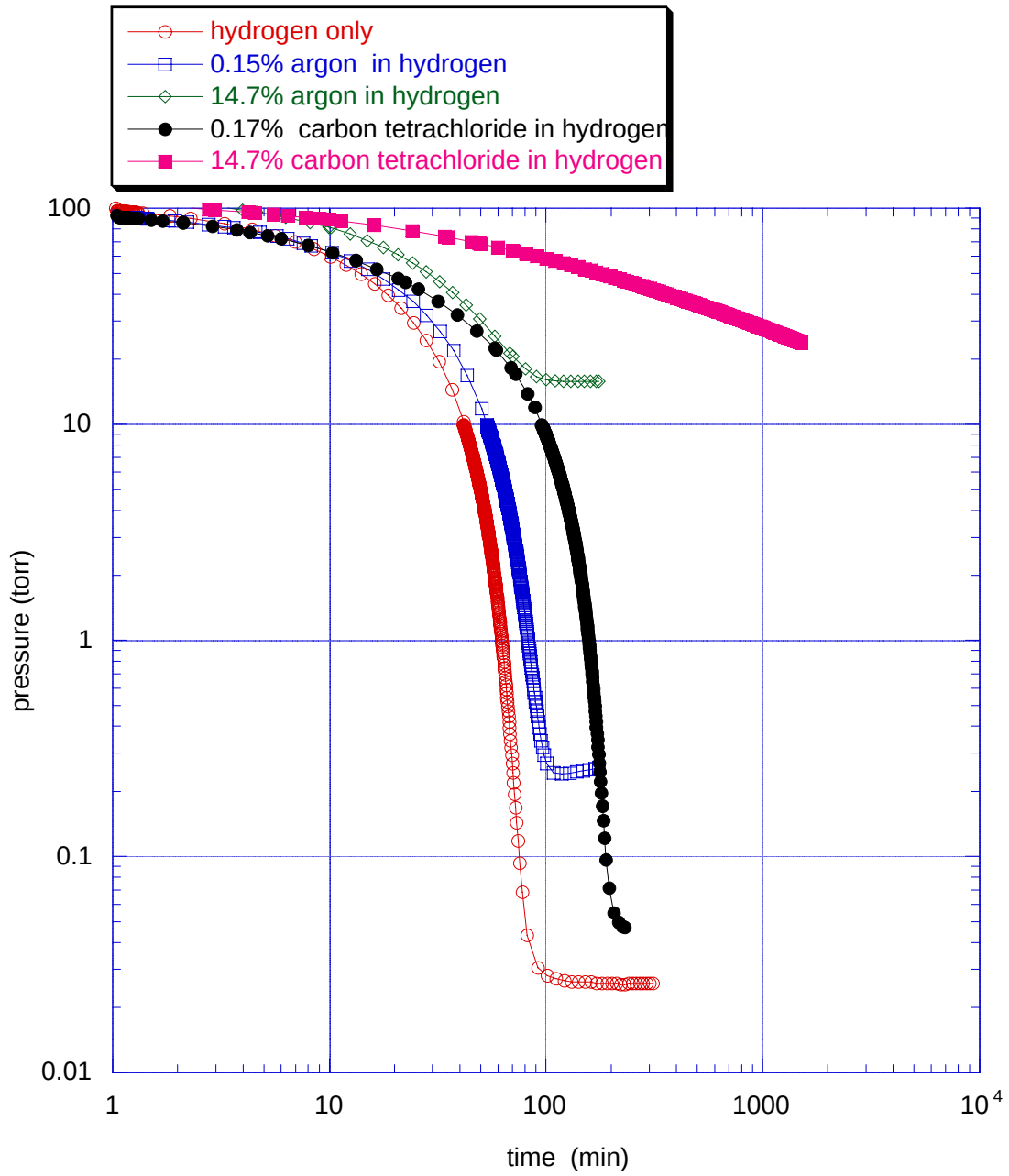

Figure 3. Pressure plot for getter competition experiments.

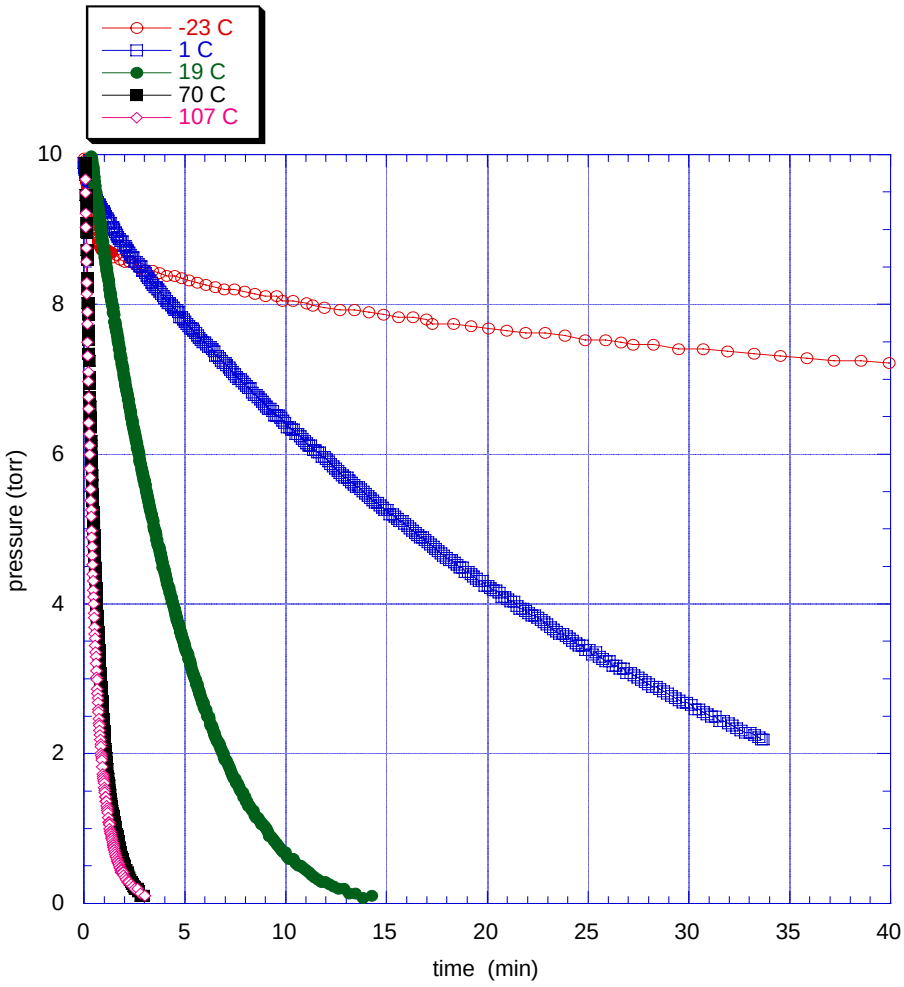

Figure 4. Pressure plot for getter A at different temperatures.

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