Improved Hydrogen Gas Getters for TRU Waste

Transuranic and Mixed Waste Focus Area – Phase 2 Final Report

M. Stone
M. Benson
C. Orme
E. Peterson
J. Kaszuba
E. Mroz
M. Haga

April 2002

Improved Hydrogen Gas Getters for TRU Waste Transuranic and Mixed Waste Focus Area – Phase 2 Final Report

Mark Stone, INEEL
Michael Benson, INEEL
Christopher Orme, INEEL
Eric Peterson, INEEL
John Kaszuba, Los Alamos
Marc Haga, Los Alamos
April 2002

Idaho National Engineering and Environmental Laboratory
Idaho Falls, Idaho 83415

ABSTRACT

Alpha radiolysis of hydrogenous waste and packaging materials generates hydrogen gas in radioactive storage containers. For that reason, the Nuclear Regulatory Commission (NRC) limits the flammable gas (hydrogen) concentration in the Transuranic Package Transporter-II (TRUPACT-II) containers to 5 vol% of hydrogen in air, which is the lower explosion limit. Consequently, a method is needed to prevent the build up of hydrogen to 5 vol% during the storage and transport of the TRUPACT-II containers (up to 60 days). One promising option is the use of hydrogen getters. These materials scavenge hydrogen from the gas phase and irreversibly bind it in the solid phase. One proven getter is a material called 1,4-bis (phenylethynyl) benzene, or DEB. It has the needed binding rate and capacity, but some of the chemical species that might be present in the containers could interfere with its ability to remove hydrogen. This project is focused upon developing a protective polymeric membrane coating for the DEB getter material, which comes in the form of small, irregularly shaped particles. This report summarizes the experimental results of the second phase of the development of the materials.

SUMMARY

This work is being performed for DOE's Transuranic and Mixed Waste Focus Area (TMFA). This project addresses the problems being encountered by the TMFA in their efforts to implement efficient getters for the TRUPACT-II containers that will limit the hydrogen gas concentrations to 5 vol% for 60 days. The focus of our activity is using polymer encapsulation technology to protect the getter and its catalyst from poisons such as volatile organic compounds (VOCs). This is a joint project between the Idaho National Engineering and Environmental Laboratory (INEEL) and the Los Alamos National Laboratory (LANL). The INEEL had the responsibility to select, screen, and coat the getter particles with the candidate membranes and then transmit them to LANL to perform the getter characterization testing.

Phase 1 accomplishments included selection of appropriate getter material by INEEL and evaluation of getter testing ability by LANL. Phase 2 focused upon getter testing.

The proposed getter formulations (coated and uncoated) were subjected to tests that determined the performance of the getters with regards to capacity, operating temperature range (with hydrogen in nitrogen and in air), hydrogen concentration, poisons, aging, pressure, reversibility, and radiation effects. The conclusions that can be made up to this point are: *1) All of the polymer coated materials performed well above the figure of merit, and 2) Even the uncoated getter performed above the figure of merit.*

The conclusions that can be stated about the getter performance relative to the programmatically specified parameters include:

- Over the complete temperature range and maximum poison concentration 5.7 kg of getter provided the required capacity and rate,
- In the temperature range of 160°F to 77°F the getter rates exceed the minimun programmatic requirement by at least 100X,
- In the temperature range of 23°F to –20°F the getter rates exceed the minimum programmatic requirements by at least 10X,
- Reducing the hydrogen concentrations from 5% to 1% in nitrogen had no significant effect on the rate,
- Reaction rates are higher in air than in nitrogen due to recombination plus gettering reactions,
- The gettering reaction was not found to be sensitive to pressure, radiation, and was shown not to be reversible, and
- Under the worst case conditions (low temperature, air, and in the presence of CCl_4), the observed rate was greater than 8X the minimum programmatic requirement.

CONTENTS

FIGURES

TABLES

ACRONYMS

CH-TRU   Contact-handled transuranic

CofC   Certificate of Compliance

DEB   1,4-bis (phenylethynyl) benzene

DOE   U.S. Department of Energy

INEEL   Idaho National Engineering and Environmental Laboratory

LANL   Los Alamos National Laboratory

NRC   U.S. Nuclear Regulatory Commission

PS   Polystyrene

PVC   Poly(vinylchloride)

SARP   Safety Analysis Report for Packaging

TRU   Transuranic

TRUPACT-II   Transuranic Package Transporter-II

VOC   Volatile organic compound

Improved Hydrogen Gas Getters for TRU Waste Mixed Waste Focus Area— Phase 2 Final Report

1. INTRODUCTION

This document reports the results of Phase 2 testing of the "Improved Hydrogen Gas Getters for TRU Waste" program for DOE's Transuranic and Mixed Waste Focus Area (TMFA) carried out by the Idaho National Engineering and Environmental Laboratory (INEEL) and Los Alamos National Laboratory (LANL).

All of the getters being investigated by all parties in this getter program use a precious metal hydrogenation catalyst to chemically react free molecular hydrogen with some type of unsaturated organic/polymeric material. Early testing showed that certain chemicals reduced the activity of the catalyst enough to warrant the investigation of ways to protect the getter system from these poisons. The approach proposed, peer reviewed, and investigated by the INEEL/LANL group provides a semipermeable barrier that allows the hydrogen through to the getter and prevents the permeation of the poison. The results for the coated getter systems are reported in this document. If a suitable encapsulant can be found, the INEEL/LANL approach has the advantage of working regardless of the amount of poison present.

Many polymers were used to encapsulate and protect the getter, 1,4-bis (phenylethynyl) benzene, or DEB, and its catalyst from poisons such as volatile organic compounds (VOCs). Phase 1 results indicated that there is no inherent reason why polymer-coated getters cannot work. The background of the project and Phase 1 results are described, followed by the Phase 2 results coupled with our recommendations.

2. BACKGROUND

2.1 Transuranic Waste Transportation Problem

The Transuranic Package Transporter-II (TRUPACT-II) was developed for the U.S. Department of Energy (DOE) primarily for shipment of contact-handled transuranic (CH-TRU) waste from DOE generator/storage sites to the Waste Isolation Pilot Plant. The TRUPACT-II was designed in accordance with the requirements for Type B packaging found in Title 10, Code of Federal Register Part 71. The Nuclear Regulatory Commission (NRC) granted a certificate of compliance (CofC) for the TRUPACT-II in 1989. The CofC specifies limits on the authorized payload in a TRUPACT-II to ensure safety during transport. These limits are based on the results of testing and analyses, which were documented in the TRUPACT-II Safety Analysis Report for Packaging (SARP) and submitted by the DOE to the NRC (NRC 1996).

The NRC has imposed a flammable gas (i.e., hydrogen) concentration limit on CH-TRU waste transported using the TRUPACT-II to minimize the potential for loss of containment during transport. This limit is set at the lower explosive limit of 5 vol% of hydrogen in air. Accident scenarios and the resulting safety analysis, developed as part of the TRUPACT-II SARP, require that this limit be met for a period of 60 days. The NRC limit of 5 vol% hydrogen applies to the innermost layer of confinement within a drum or standard waste box.

Hydrogen gas generation and accumulation is the result of alpha radiolysis of hydrogenous waste and packaging materials coupled within waste packaging configurations. The combination of high activity wastes with multiple layers of packaging results in significant quantities of wastes that do not meet transportation requirements for hydrogen gas concentration. Payload expansion to support the shipment of high activity wastes drives the use of hydrogen gas getters in the TRUPACT-II. Hydrogen gas getters are solid materials that irreversibly remove hydrogen from the gas phase. One potential solution for a waste drum over 0.5 watts is to use a getter to allow for shipment. These wattage levels are seen primarily in two waste types: the plutonium-238 (heat source plutonium) wastes at LANL and Savannah River Site, and americium-contaminated wastes at Hanford, INEEL, Oak Ridge National Laboratory, and Rocky Flats Environmental Technology Site.

Another solution for these high activity wastes is to repackage the waste to a configuration that has two layers of confinement with filter vents on the bagging material. The addition of a hydrogen getter material then allows for up to 5 grams of heat source plutonium in the drum. This scenario results in minimal volume expansion for these waste streams.

2.2 Technology Concept and Function

Preferred hydrogen getters are solid materials that scavenge hydrogen (H_2) from the gas phase and chemically and irreversibly bind it in the solid state. 1,4-bis (phenylethynyl)benzene (DEB) (Figure 1) belongs to a class of compounds called alkynes, which are characterized by the presence of carbon-carbon triple bonds. The triply-bonded carbon atoms in alkyne compounds will, in the presence of suitable catalysts such as palladium (Pd), irreversibly react with hydrogen to form the corresponding saturated alkane compounds. DEB, as a hydrogen getter, does not require the presence of oxygen to be effective. DEB does not produce water as a reaction product when reacting with the hydrogen. However, in the presence of oxygen, recombination reactions on the Pd catalyst will produce water in addition to hydrogenating the dialkyne. Thus, the material acts as both a getter and recombiner in the presence of air. The getters also have been found to be hygroscopic in air environments. Thus, exposure of the getter to oxygen and water needs to be minimized.
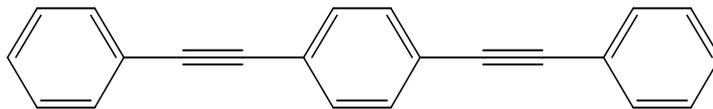
Figure 1. Structure of 1,4-bis (phenylethynyl) benzene.

Many potential hydrogen gettering compounds and formulations have been tested (Sheppod *et al.* 1989; Smith and Sheppod 1990). The best performance has been achieved with DEB, a nontoxic, nonmutagenic, crystalline solid. Because DEB is a dialkyne (containing two triple bonds), one mole of DEB reacts with 4 moles of hydrogen (2 moles of hydrogen react to form the corresponding dialkene, an additional 2 moles of hydrogen react to form the dialkane). DEB melts at +179 °C, whereas the fully hydrogenated product melts at +87 °C. The standard formulation for the "DEB getter" is a mixture of 75 % DEB and 25 % carbon catalyst (5 % Pd on carbon). The production process is quite simple: the two materials are mixed together in a ceramic jar mill for several hours after which the DEB getter is ready for use. It has been shown to be stable in the absence of hydrogen for up to 18 months (at +70 °C, under N_2). The uncoated getter granules are shown in Figure 2.

Figure 2. Photograph of the uncoated DEB getter (X20).

The DEB getter reacts rapidly, exothermically (~30 kcal/mole H_2), and irreversibly with hydrogen. It has a capacity of 240 to 330 cm^3 hydrogen per gram. The reaction is nearly stoichiometric and proceeds to >90 % of the theoretical capacity. In experiments in a nitrogen atmosphere with a hydrogen addition rate of about 10^{-3} cm^3/sec, the hydrogen concentration was maintained at less than 5 ppm until the getter had reacted to >90 % of its theoretical capacity. The reaction rate with hydrogen is temperature-dependent and proceeds more rapidly as the temperature is increased.

In FY98, experiments were performed at LANL to investigate whether other compounds expected to be present in the headspace of TRU waste containers would affect the performance of the DEB getter. These tests showed that DEB was unaffected by toluene, hexane, acetone and methanol. However, carbon monoxide (CO) and several chlorinated volatile organic compounds (VOCs) (e.g. carbon tetrachloride,

3

trichloroethylene, trichloroethane, chloroform, and methylene chloride) did inhibit the reaction of hydrogen with DEB. The figure of merit for hydrogen removal in the inner containment volume of the TRUPACT-II container had not been determined at that time, therefore, the impact of VOCs on DEB reaction could not be quantitatively assessed. It was determined, at the time, that a solution to the poisoning problem must be found for DEB to maintain its effectiveness for removal of hydrogen from TRU waste. Microencapsulation of the DEB particles was proposed, peer reviewed, and studies initiated to evaluate coated DEB as a potential solution to this pressing problem for DOE.

2.3   Current State of Development

The DEB-Pd/C formulation has been successfully incorporated into several forms, including powder, pellets, shaped polyethylene composite, a urethane adhesive film, and a castable room temperature-vulcanizing (RTV) silicone. The material has been in regular production for use in DOE nuclear weapons components and assemblies since 1977. However, the needs of these other applications are quite different from the TRUPACT II.

Microencapsulation technology is not new. The technology forms the basis for many of the commercial time- or pressure-released components found in the food, drug, perfume, and agricultural industries. Commercial applications of microencapsulation include carbonless carbon paper, time-release pharmaceuticals, herbicides, scents, catalysts, and polymerization initiators. Application of microencapsulation technology to hydrogen getters for the nuclear industry is a new concept and is the reason for this project.

2.4   Technology Improvements Needed

There are two aspects to achieving the desired goal. One is the development of useable microencapsulation methods and techniques and the other is performing the microencapsulation with materials that possess the desired permeation properties. Investigating both of these areas is essential because new materials are needed to meet the requirements of the TMFA. As possible encapsulating materials are identified, it will be necessary to develop the methods needed to apply them (either as single layers or multiple layers) surrounding the getter. It will also be necessary to measure the permeabilities of the as-produced layers. The technology improvements gained from this work will make it possible to deploy the hydrogen getters in many applications and will make it possible to safely transport materials in the TRUPACT-II containers.

2.5   Phase 1

The thrust of this project is to microencapsulate the DEB particles in hydrogen-permeable polymer coatings. Our approach has been three-phased: 1) choose the best coating material(s) based on hydrogen permeability tests, 2) investigate methods for encapsulating the DEB/Pd-C containing particles and, 3) transfer the formation process to a larger scale. Phase 1 was a feasibility study consisting of two prime components: *1) can the irregular shaped getter particles be coated with thin dense films of hydrogen permeable membranes?, and 2) will the coated particles show the needed gettering activity level to function in the TURPACT-II containers?* Phase 1 objectives were achieved. Solution and spray methods were used for encapsulation; spray coating was found to be more efficient and versatile than solution methods. Permeabilities of several gases were measured by the time-lag method for a variety of polymers. Three polymers, polyvinyl chloride (PVC), polystyrene, and polysulfone, were chosen as the initial encapsulation materials based on their hydrogen permeabilities and on ease of processing. Eight encapsulated DEB samples, containing PVC, polystyrene, both PVC and polystyrene, or polysulfone,

were tested at LANL for their hydrogen getter properties in a dynamic (flowing) system. The polystyrene-containing materials performed the best.

2.5.1   Polymer Permeability

2.5.1.1   Pure Gas Testing. The first task of Phase 1 was to select potentially useful polymers. Membranes having thicknesses in the range of 50 to 200 microns were tested in a pure (single) gas facility at the INEEL (Figure 3). The primary focus of the pure gas test screening has been to determine if the polymers being considered have a H_2 permeability high enough to allow H_2 to pass through the polymer at the same rate as it is produced, $\sim5 \times 10^{-10}$ cm x cm^3/sec x cm^2cm Hg. Each polymer was initially tested using six gases that might be seen in a container: He, H_2, N_2, O_2, CH_4, CO_2. All of the pure gas tests were performed at 30 °C and 30 psi feed gas pressure. Figure 3 shows the set-up for the tests. A membrane is evacuated on both sides, then isolated, then one side is exposed to a feed gas, and the pressure increase as a function of time on the permeate side gives the information necessary to calculate the permeabilities. The results of all Phase 1 and 2 pure gas testing are given later in the Phase 2 results. Some of the later polymers were tested against a reduced set of gases. Several polymers met the requirements.
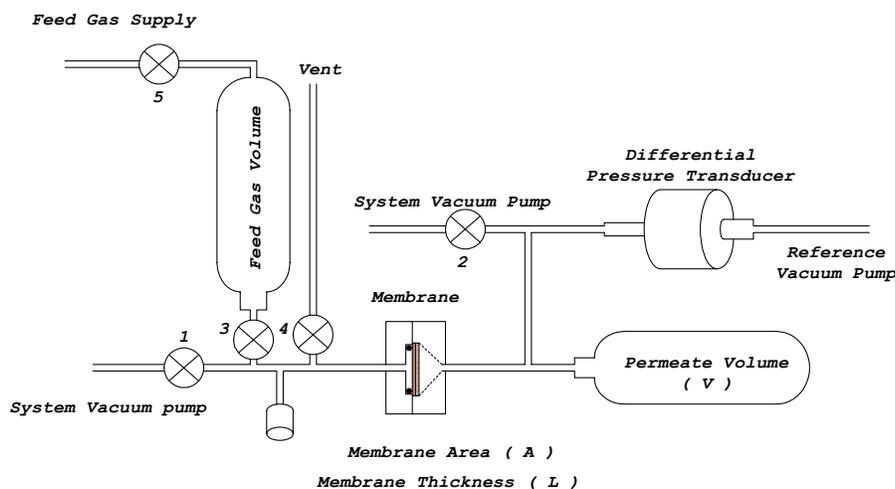
Figure 3. Schematic of the pure gas screening test apparatus.

2.5.1.2   Mixed Gas Testing. The mixed gas screening test differs from the pure gas test in two ways. 1) It is a flowing test where the pure gas is a stagnant test., and 2) the feed gas contains mixtures of gases. In the mixed gas experiments a pressurized feed gas flows at a constant rate over the surface of the membrane. Any permeant gases are entrained in a sweep gas that transports them to a set of gas chromatographs (GC) for analysis. The schematic is shown in Figure 4. Since some of the screening studies were continued into Phase 2, all of the mixed gas test results are reported in the Phase 2 section. The importance of the mixed gas test is that it allows the use of a more realistic set of gases, including some of the suspected catalyst poisons.
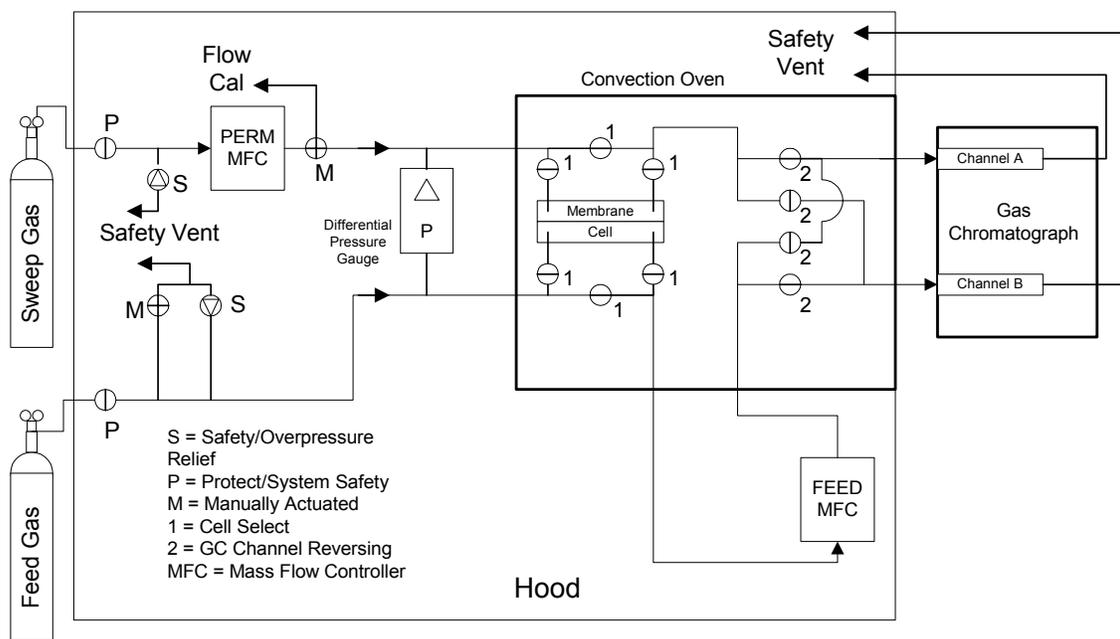
Figure 4. Schematic of the mixed gas test system.

2.5.2   Coating Technique

All method development experiments were carried out using carbon particles in place of the more expensive DEB particles. Carbon is the support for the catalyst in the DEB particles, making activated carbon an excellent test case while the coating techniques were developed. Spray coating is a convenient method, but it is limited to polymers that are soluble in volatile solvents. Melt thermoforming offers another technique for polymers that are not soluble in the volatile solvents necessary for spray forming.

2.5.2.1   Solution Methods. Complex coacervation was the only solution coating technique attempted. Gelatin and gum arabic were used as the coating material, with glutaric dialdehyde as the crosslinking agent. A large amount of polymer was needed to completely coat the particles due to microsphere formation. Solution techniques are generally used to encapsulate a liquid with a microsphere. After a microsphere is formed (with no particle inside), that material can no longer coat a solid particle. When a large excess of polymer was not used, the particles were not completely coated. Spray coating was being investigating simultaneously, and was found to be much more efficient and versatile for coating solids, so solution methods were not continued.

2.5.2.2   Spray Coating. Spray coating has several advantages over solution methods for this application. Although DEB is not very soluble, it is slightly soluble in specific solvents, such as toluene and acetone. Spray coating does not allow prolonged exposure of the DEB to the solvent, preventing DEB from dissolving and being separated from the catalyst and support. Spray coating also has the advantage of versatility. Solution methods are much more restricted in the polymers that can be applied. For example, complex coacervation requires a positive and a negative component (gelatin and gum arabic, respectively). Also, optimal conditions for obtaining a specific coating thickness and for separating and drying the particles without clumping are harder to determine for solution methods. Spray coating dries the particles while the polymer is being applied, and, in general, if a polymer can be dissolved it can be spray coated.

Commercial spray coaters require large quantities of material, such as >500 g. The ability to coat gram quantities was needed for this project, so a small-scale spray coater was constructed. Two types of spray coaters are used industrially. In one type, the solution is sprayed down onto a fluidized bed from the top; in the other, the solution is sprayed from the bottom (the Wurster Spray Coater, Figure 5). Both setups were constructed to coat the small quantities of materials needed for testing. The top-spray system coated the particles, but not very efficiently and only with very thin coatings. The Wurster-type coater was found to be very efficient, and could quickly coat up to 5 gram quantities. The spray coater is pictured in Figure 6.

2.5.3   Characterization

2.5.3.1   Scanning Electron Microscopy (SEM). The most direct way to examine the physical nature of the coated particles was to look at them under the SEM. Some of the particles were used as produced and others were cut in half so the profile of the coating could be used to measure the thickness and the continuity of the membrane, Figure 7.
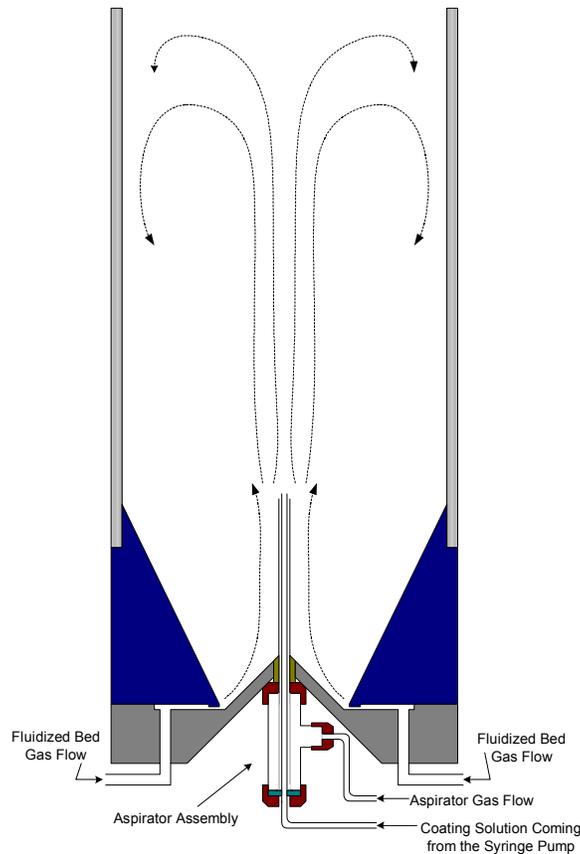
Figure 5. Schematic Diagram of Wurster-Type Coater. The aspirator assembly introduces the polymer solution as a fine mist, while the fluidized bed gas flow keeps the particles circulating through the mist. The circulation keeps the particles from sticking together, while the combined gas flows quickly evaporate the solvent.

Figure 6. Picture of Spray Coater. The plastic tube has been removed for clarity.
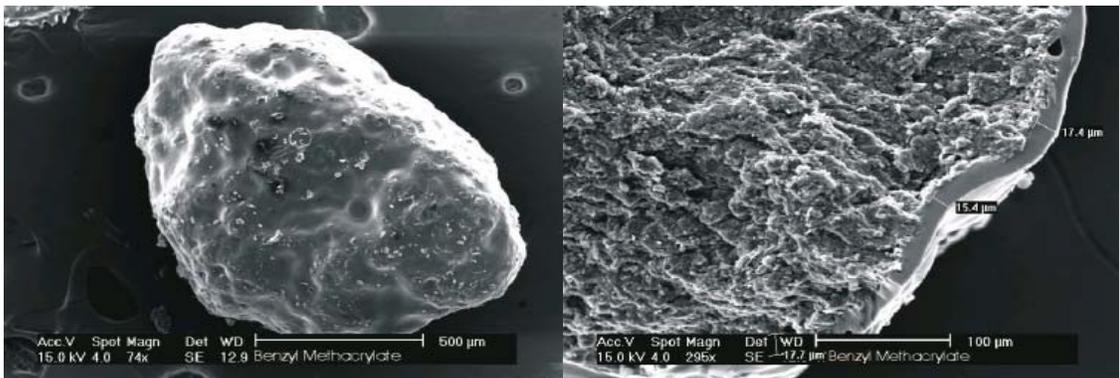
Figure 7. SEM photographs of DEB coated with polybenzyl methacrylate. The image on the left shows an entire coated particle and the image on the right shows a particle that has been cut in half.

2.5.3.2 ***Optical Fluorescence Microscopy.*** It is important to be able to check the continuity of the spray coated polymer layer. Optical fluorescence microscopy worked well for this purpose. A small quantity of fluorescein was dissolved into a polymer solution. This mixture was spray coated onto the particles in the usual fashion. Next, the reddish appearing particles were potted in an epoxy and a section containing the coated particles was cut through and polished. Finally, the prepared sample was placed under an optical fluorescence microscope and with the proper filters and lenses the coating was subjected to a wavelength of light that caused the dye containing polymer coating to fluoresce and the photograph in Figure 8 was taken. It shows the nicely coated, irregular shaped surface the DEB particle.
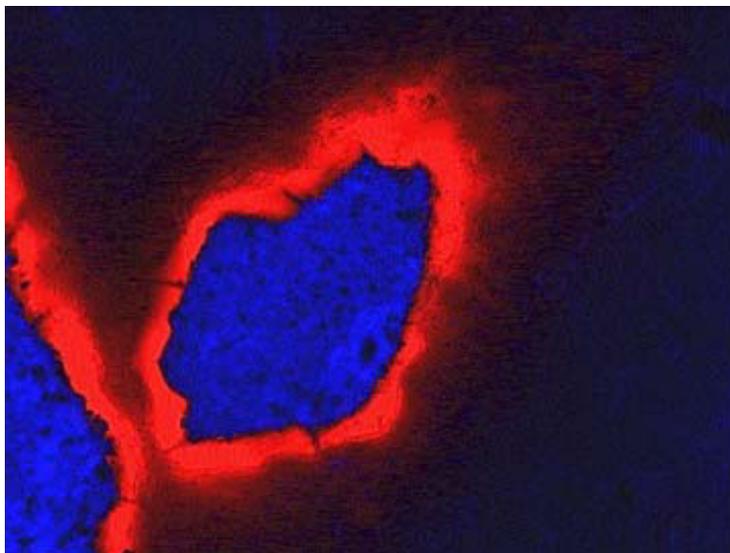
Figure 8. Optical fluorescence microphotograph of a polymer encapsulated DEB particle. The orange/red is the polymer coating fluorescing and the blue is the DEB fluorescing.

2.5.3.3 H_2 Getter Properties of DEB Samples. Eight samples were sent to LANL and tested in Phase 1. There were differences among the coated materials showing the coating was involved. Some were unsuitable and others worked fine, indicating the approach was valid and proceeding to Phase 2 was appropriate.

2.5.3.4   Coating Thickness. The percent by volume of polymer on the DEB particle is needed to accurately determine the efficiency of the polymer/DEB combination, and is determined from the coating thickness. The efficiency (total amount of hydrogen scavenged) will depend on the amount of DEB, so the polymer weight must be subtracted from the sample weight. To ensure that the polymer is not interfering with the hydrogen scavenging capability of the DEB, the efficiency must be determined for each sample. The rate of hydrogen scavenging will vary depending on the coating and the thickness. Assuming the efficiency of the DEB is not decreased, the rate of hydrogen scavenging will be the performance indicator for the polymer coatings. Most of the coatings were in the 5 to 40 micron range.

Coating thickness was determined using SEM. For each sample, at least three measurements were used to determine the average thickness. If one measurement was significantly different from the others, more measurements were used for the average. Table 1 lists the % coating by volume for each sample, along with the numbers used to calculate the % volume. The particle size used in the calculations is 700 μm (particle volume = 180,000,000 μm^3). The average particle size was determined with a sonic sifter, using 8 sieves between 300 and 1180 μm. The calculations assume spherical particles (see Figure 9).

Table 1. Percent volume of polymer on particle.

Sample[a] No.	Average coating thickness (μm)	R_1 (μm)	R_2 (μm)	Coating Volume (μm³)	Total Volume (μm³)	% Coating Volume
PS (25 ml)	9.3	359.3	350	14763910	194267244	7.6
PS (50 ml)	25.1	375.1	350	41454589	220957922	18.8
PVC (50 ml)	16.6	366.6	350	26715011	206218344	13.0
PVC (100ml)	27.8	377.8	350	46260435	225763768	20.5
PVC/PS (50ml; mixture)	15.9	365.9	350	25591922	205095255	12.5
PVC layer then PS layer	32.3	382.3	350	54362982	233866315	23.2
PS layer then PVC layer	39.8	389.8	350	68527287	248030620	27.6
Polysulfone (50ml)	12.8	362.8	350	20423101	199926434	10.2

[a]PS=polystyrene PVC=polyvinyl chloride
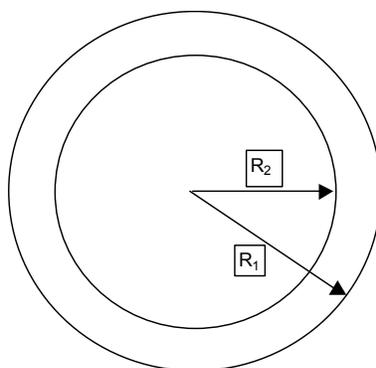
Figure 9. Particle model for calculations.

2.5.4   Phase 1 LANL Testing Results

Dynamic testing is performed by flowing a gas mixture (typically 5 % hydrogen in nitrogen) over a sample of the getter material at a constant temperature. A photograph of the experimental set up appears in Figure 10. The concentration of the hydrogen passing out of the system as a function of time is recorded. When the experiment is initiated using the uncoated getter, a rapid rise in hydrogen is observed first in the outlet gas (Figure 11, *the time axis is from right to left*). This reaches a peak after about 5 minutes and then the concentration starts to decline to a minimum followed by a long, slow, gradual increase in concentration that asymptotically approaches the concentration of the inlet gas. The interpretation is that the initial peak represents an activation or absorption step wherein hydrogen is being loaded onto the catalyst surface. When enough hydrogen gets loaded, the reaction rate with the getter is faster than the absorption kinetics and the concentration in the exit gas stream declines to a minimum. The concentration of hydrogen in the exit gas stream gradually approaches the concentration of the inlet gas as the getter is consumed and the reaction rate declines.

10
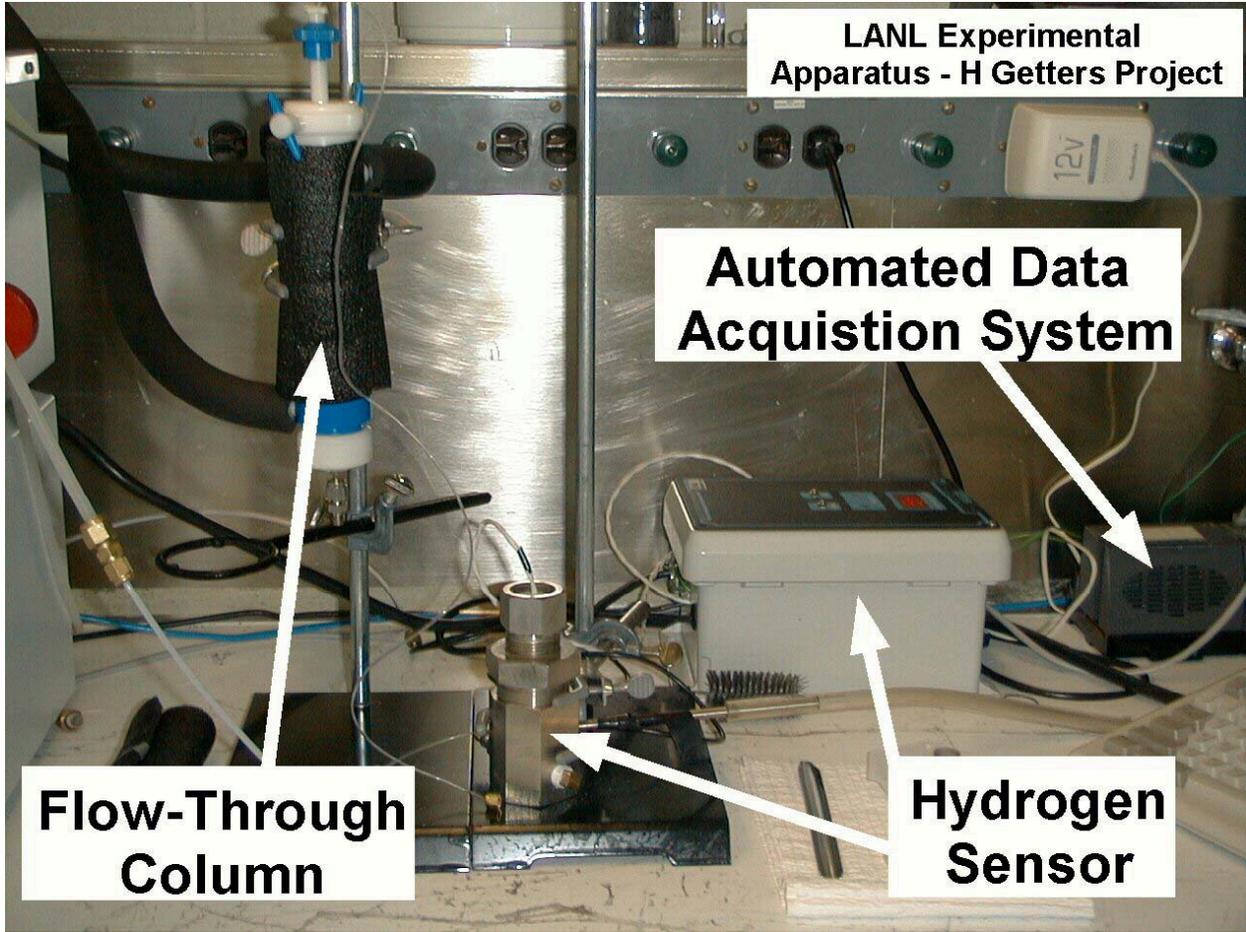
Figure 10. Photograph of the LANL getter testing apparatus. The automated data acquisition system that is pictured was installed during Phase 2 Testing. A chart recording system was used in Phase 1.
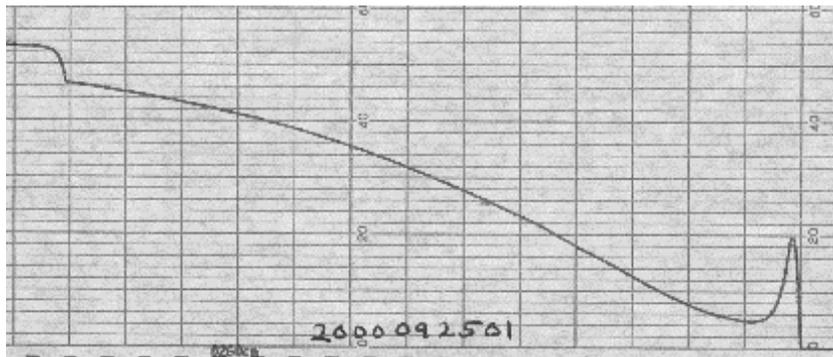
Figure 11. Uncoated getter response in dynamic testing. The time axis is from right to left; each division on the chart paper is 10 minutes. The initial peak can be seen, followed by the gradual increase in hydrogen concentration as time goes by. The final increase at the left end of the chart is where the operator directs the input gas directly into the detector for calibration.

To evaluate the performance of the coated getters, a parameter called T50 was calculated from a strip chart record as shown in Figure 11. T50 is defined as the time required for one gram of material to react with 50 % of its stoichiometric capacity when exposed to a gas mixture of 5 % hydrogen in nitrogen flowing through a column of the getter material at 10 cm^3-atm/min at constant temperature. The strip chart is optically scanned and digitized. The cumulative amount of hydrogen reacted as a function of time is calculated and T50 is determined from the mass of the sample and the known capacity of DEB for hydrogen (241 cm^3-atm H_2/gram).

The plot for polystyrene (PS) coated getter reacting with hydrogen, Figure 12, has the same overall shape and features as the plot for the uncoated getter but the time frame is longer. This reflects the fact that the coating slows the overall process, but does not change the final outcome.

The plot for hydrogen reacting with a PVC-coated getter material, Figure 13, is substantially different from the previous two. Notice that at the start of the experiment the concentration of the hydrogen increases rapidly so that in just a few minutes it has reached the H_2 inlet concentration, indicating that the PVC-coated material is unsuitable for this application.

The hydrogen permeability of PS is about 25 whereas that of PVC is about 6. The difference in the permeabilities may, in part, be due to the differences in the morphologies of the polymers, to their different densities (the more permeable PS has a density of approximately 1.1 while that of PVC is 1.4), or to the effectiveness of the coatings.
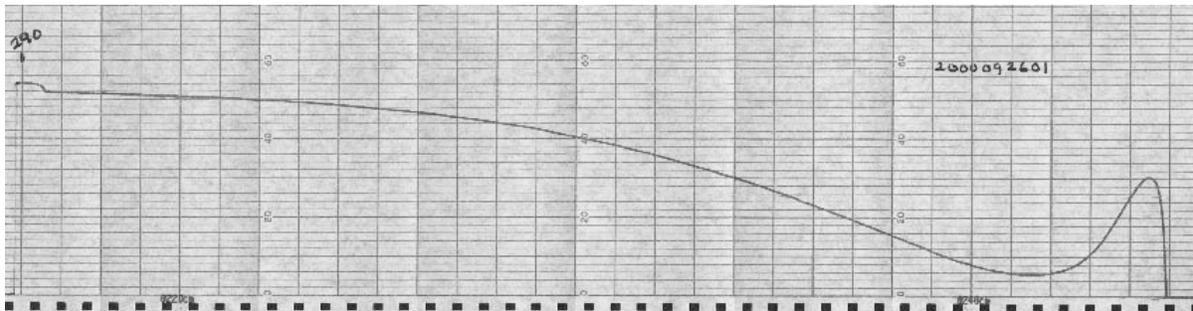
Figure 12. Polystyrene coated getter in dynamic testing. Time axis is from right to left.
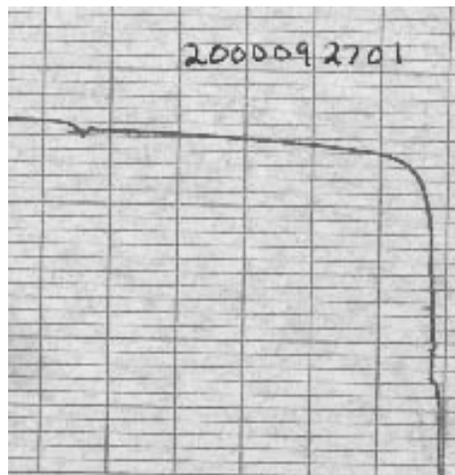
Figure 13. Poly (vinylchloride) coated getter in dynamic testing. Time axis is from right to left.

A complete test consists of two experimental runs, a Control Run and a Test Run. The Control Run exposes the material to a mixture of 5 % H_2 in N_2 with no CCl_4. The Test Run exposes the material to a mixture of CCl_4 vapors in 5 % H_2 in N_2. Comparison of the T50 values for each run shows the effect of the coating on hydrogen gettering performance in the presence of a known poison, CCl_4.

The thinnest coating of PVC (i.e. materials #3 or #5 in Table 1) was sufficient to prevent any permeation of hydrogen through to the active getter material and yielded curves such as can be seen in Figure 13. Experiments conducted at both 20 and 40 °C obtained the same result. No further tests were conducted with PVC containing materials.

All of the experiments discussed above were conducted with a gas mixture of hydrogen in nitrogen. In this environment, the only reaction mechanism removing hydrogen is addition of hydrogen atoms across the unsaturated bonds of the DEB molecule. In a hydrogen-air mixture, the addition reaction is supplemented by the catalytic recombination reaction forming water. We estimate that in an air environment, about 13 % of the hydrogen reacting with DEB is removed via the recombination reaction and the remaining 87 % undergoes the addition reaction. Experiments showed that the recombination reaction is also rapidly poisoned by CCl_4. A summary of tests performed in Phase 1 is presented in Table 2.

Table 2. Phase 1 test results.

LANL Run ID	INEEL Sample ID	Polymer	CCl$_4$ (ppm)	Moles H$_2$/s/g at 50% Saturation[a]	Rate Ratio[b]	DEB required for 62.2 moles H$_2$ (g)[c]	Reaction Rate at 50% Saturation (mol/s)[d]	Is Reaction Rate >1.2E-05 mol/s?[e]
2000100501	DEB	None	0	1.20E-06		5,765	6.92E-03	Yes
2000101101	DEB	None	500	3.19E-07	0.27	5,765	1.84E-03	Yes
2000092601	INEEL#1	Polystyrene	0	8.40E-07		5,765	4.84E-03	Yes
2000101001	INEEL#1	Polystyrene	500	3.18E-07	0.38	5,765	1.83E-03	Yes
2000092704	INEEL#2	Polystyrene	0	4.63E-07		5,765	2.67E-03	Yes
2000101901	INEEL#2	Polystyrene	500	2.25E-07	0.49	5,765	1.30E-03	Yes
2000100402	INEEL#8	Polysulfone	0	7.70E-07		5,765	4.44E-03	Yes
2000100601	INEEL#8	Polysulfone	500	1.68E-07	0.22	5,765	9.68E-04	Yes
2001040901	15493-133	Poly(styrene-co-acrylonitrile)	0	4.48E-07		5,765	2.58E-03	Yes
2001040902	15493-133	Poly(styrene-co-acrylonitrile)	500	8.15E-08	0.18	5,765	4.70E-04	Yes
2001041001	15493-134	Poly(styrene-co-methacrylate)	0	1.85E-07		5,765	1.07E-03	Yes
2001041201	15493-134	Poly(styrene-co-methacrylate)	500	8.89E-08	0.48	5,765	5.12E-04	Yes
2001032003	15493-136	Polymethylmethacrylate	0	5.02E-07		5,765	2.89E-03	Yes
2001032602	15493-136	Polymethylmethacrylate	500	1.02E-07	0.20	5,765	5.88E-04	Yes
2001041002	15493-137	Polyisopropylmethacrylate	0	1.85E-07		5,765	1.07E-03	Yes
2001041101	15493-137	Polyisopropylmethacrylate	500	6.88E-08	0.37	5,765	3.97E-04	Yes
2001032102	15493-138	Polybenzylmethacrylate	0	1.80E-07		5,765	1.04E-03	Yes
2001032703	15493-138	Polybenzylmethacrylate	500	1.15E-07	0.64	5,765	6.63E-04	Yes
2001032201	15493-140	Poly(styrene-co-allylalcohol)	0	3.09E-07		5,765	1.78E-03	Yes
2001032802	15493-140	Poly(styrene-co-allylalcohol)	500	6.00E-09	0.02	5,765	3.46E-05	Yes
2001051501	15664-14	Polyvinylidine difluoride (Kynar)	0	1.38E-07		5,765	7.96E-04	Yes
2001051601	15664-14	Polyvinylidine difluoride (Kynar)	500	8.05E-08	0.58	5,765	4.64E-04	Yes

Table 2. (continued).

LANL Run ID	INEEL Sample ID	Polymer	CCl$_4$ (ppm)	Moles H$_2$/s/g at 50% Saturation[a]	Rate Ratio[b]	DEB required for 62.2 moles H$_2$ (g)[c]	Reaction Rate at 50% Saturation (mol/s)[d]	Is Reaction Rate >1.2E-05 mol/s?[e]
Duplicates								
2001060601	15664-17-1	Polybenzylmethacrylate	0	9.00E-08		5,765	5.19E-04	Yes[f]
2001060602	15664-17-2	Polybenzylmethacrylate	0	3.50E-08	0.39	5,765	2.02E-04	Yes[f]
2001060701	15664-18-1	Poly(styrene-co-methylmethacrylate)	0	2.36E-07		5,765	1.36E-03	Yes
2001060702	15664-18-2	Poly(styrene-co-methylmethacrylate)	0	1.35E-07	0.57	5,765	7.78E-04	Yes
2001060801	15664-19-1	Polystyrene	0	3.77E-07		5,765	2.17E-03	Yes
2001060802	15664-19-2	Polystyrene	0	3.73E-07	0.99	5,765	2.15E-03	Yes
2001060901	15664-20-1	Polyvinylidine difluoride (Kynar)	0	1.16E-07		5,765	6.69E-04	Yes
2001061501	15664-20-2	Polyvinylidine difluoride (Kynar)	0	2.58E-08	0.22	5,765	1.49E-04	Yes

NOTES:

a. Moles H$_2$/s/g at 50% saturation is the instantaneous specific reaction rate when the getter sample was at 50% of its stoichiometric capacity for H$_2$. Temperature: 40 °C

b. Rate Ratio is the ratio of rates in the previous column. The closer to unity, the better the coating is performing.

c. DEB required for 62.2 moles H$_2$ is the maximum amount of DEB needed to react with the worst case amount of hydrogen that would be generated within a TRUPACT-II container. It is derived from the reaction stoichiometry.

d. Reaction Rate at 50% Saturation (mol/s) is the product of CCl$_4$ (ppm) and Moles H$_2$/s/g at 50% saturation. It is an estimate of the instantaneous reaction rate of 5765 g of DEB at 50% saturation.

e. Comparison against the worst cast generation rate, 1.2E-5 mol/s. Note that even materials whose performance is severely impacted by CCl$_4$ (e.g. 15493-140), the large mass of material present still keeps the instantaneous reaction rate at 50% saturation greater than the hydrogen generation rate.

f. 25% saturation

15

3.   PHASE 2

3.1   INEEL Screening Test Results

Table 3 summarizes the pure gas test screening. A wide variety of hydrogen permeabilities were observed. These tests were performed at 30 °C.

Table 3. Hydrogen-getter polymer testing summary.

Polymer	Permeability (barriers, or $\times 10^{-10}$ cm x cm^3/(sec x cm^{2}cm Hg))					
	H_2	He	N_2	O_2	CH_4	CO_2
PTMSP Poly trimethyl silylpropyne	13244	5942	2899	6131	6464	24492
PDMS Poly dimethyl silicone	565	316	255	497	761	2318
PVC/Unplasticized Poly(vinylchloride)	6.4	7.7		1.1	0.3	1.2
PE/Bag Polyethylene	17.3	11.1	4.2	6.3	7.7	17.9
Polysulfone MW = 26K	12	10.5	0.8	1.7	0.4	6
Polysulfone MW = 35K	11.3	13.3	1.8	2.6	0.1	3.4
Poly(ethylene terephthalate) pop bottle	3.7	6.2	5.1	5	6.7	6.1
Poly methyl methacrylate MW = 350K	2.4	13		3.3	0.6	0.6
Polystyrene (weigh boat)	25.4	19.5	0.5	2.3	0.7	3.2
Polystyrene, MW = 280K	27.1	0.63	0.47	0.39	1.21	16.4
PVC viscosity = 0.62	4.59	4.55	0.16	0.37	0.22	0.7
PVC viscosity = 1.02	5.3	1.28	0.52	0.64	0.38	1.08
Poly bis(trifluoroethoxy) phosphazene	101.9		43.6	77.9	78.1	282
Poly bis(p-fluorophenoxy) phosphazene	5.84		0.43	1.44	0.91	9.46
Eypel F (fluorinated alkoxy substituted phosphazene)	79.9		32.2	64.9	40.6	375.6
CMS-3 (perfluoro amorphous copolymer)	996		170	403	113	986
Polystyrene co-methyl methacrylate	73.10				37.05	51.40
Polystyrene co-acrylonitrile	12.10				3.00	9.25
Polyvinyl butyral	10.95				1.15	8.05
Poly styrene co-butadiene	8.15				2.30	14.85
Polyvinyl acetate	14.65				0.80	11.95

The results of the mixed gas tests are given in Table 4.

Table 4. Tabulation of the mixed gas test results.

Polymer	Permeability (Barriers)		Perm Selectivity	
	Hydrogen	Carbon Tetrachloride	H_2/CCl_4	CCl_4/H_2
Poly(dimethyl Siloxane) PDMS	375 - 425	10000 - 15000	0.032	31.25
Polystyrene	21.4	24000	0.001	1121.5
Poly(vinylidene Fluoride) Kynar	2.5	9.4	0.266	3.76
Poly(benzyl methacrylate)	2.8	20.5	0.137	7.321
Poly(propylene)	3.5	1.65	2.121	0.471
Poly(benz-imidazol) PBI	1.8	1.7	1.059	0.944
Poly(ethylene vinyl alcohol) EVAL	0.11	1.2	0.092	10.909
Poly(ethylene terephthalate) PET	0.13	0.45	0.289	3.462
CMS-3 perfluoro amorphous copolymer	169.6	9.2	18.435	0.054
Poly(butadiene)	68.4	3644.5	0.019	4.572
Poly(p-sec-butyl, p-methoxy, o-allyl) phenoxy phosphazene, Lot# Z-1009-A	8.6	5.98	1.438	0.695
Poly(trifluoroethoxy) phosphazene 1% o-allyl, Lot# TE1-78	77.8	190.7	0.408	2.451
Eypel-F Mixed fluoroalkoxy phosphazene	61.9	283	0.219	4.572
CMS-3 cast in house from perfluorohexane	533.4	16.6	32.133	0.031
Polyethylene	45	79	0.570	1.756

3.2   Alternative Packaging

Some of the tested polymers that showed good permeability values are materials not particularly amenable to spray coating due to their insolubility in suitable solvents or the solvents are very expensive. A number of variations of heat and solvent sealing of these types of polymer films was conducted to produce small bags containing the getter. The advantages of the bags are that they are simple to make and they form nice packages that are easily handled. The disadvantage is that the surface absorption area is significantly less than the individually coated particles. Nevertheless, several packages containing DEB were produced and successfully tested making this a viable getter containment alternative for highly permeable polymers.

Figure 14. Heat sealed getter packet.

3.3 H_2 Getter Properties of DEB Samples

The samples considered to have the best properties were sent to LANL for H_2 getter property testing and are listed in Table 5. For the Phase 2 testing, a new batch of DEB getter was purchased and new polymer coated samples were produced, all from the same batch of DEB. The Getter was purchased from Honeywell FM&T, P/N 1473067-000, Name: DEB Getter, Granulated PRJ049755-001, Lot No. X245, Quantity: 200 grams, Date of Manufacture: 10/22/01, and received 10/30/01. Two samples made from the Phase 1 batch of getter were included for comparison; 6 and 7 in Table 5.

Table 5. A listing of the getter samples sent to LANL for testing.

	Coating
1	None: uncoated DEB getter to serve as a control.
2	Polystyrene
3	Poly styrene-co-methylmethacrylate
4	Poly vinylidine fluoride (Kynar™)
5	CMS-3™ a perfluorinated amorphous copolymer
6	Poly benzyl methacrylate
7	Poly iospropyl methacrylate

4. LANL TEST RESULTS

4.1 General Outline for the testing

The testing was performed in accordance with the TWFA coordinated Consolidated Test Plan that resulted from a meeting with all parties involved. The document describes the parameters that are to be measured and which parties would do the measurements. It gave the detail necessary to determine what ranges and bracketing values that needed to be produced in order to have a sufficient set of data to determine if the various formulations of the getters met the requirements. The following sections provide the results of those tests.

4.2 Testing Observations and Discussion

Phase 2 tests were performed in accordance with the requirements of the Consolidated Test Plan for Hydrogen Getters (Revision 3, December 20, 2001). Phase 2 dynamic testing was performed in the same manner as in Phase 1. The chart recording system employed in Phase 1 was replaced by an automated data acquisition system (Figure 10) midway through Phase 2. The "T50" parameter used in Phase 1 was refined and modified in Phase 2 per the Test Plan. "T50" was replaced with a more meaningful evaluation of getter performance, the hydrogen removal rate at 50% capacity. The dynamic test apparatus measures hydrogen removal rates in moles of hydrogen per second per unit mass (mol H_2 s^{-1} kg^{-1}). As stated in the Test Plan, hydrogen absorption rates will be expressed in these same units.

The getter test program is designed to fulfill the following programmatic requirements:

1. Minimum rate for hydrogen removal of 1.2×10^{-5} mol H_2 s^{-1} for 60 days.

2. Sufficient getter material within the TRUPACT-II to ensure that no more than 50% of getter material is consumed during the 60 days.

3. Adequate hydrogen removal rate from the getter reaction in the absence of the recombination reaction of hydrogen to produce water.

This conservative approach provides a measure of safety for waste shipments by ensuring that sufficient getter material is present and by not taking credit for the recombination reaction. The rationale for measuring and reporting the hydrogen removal rate at 50% getter capacity is thus derived. The unit specified in the Test Plan for the minimum rate of hydrogen removal (mol H_2 s^{-1}) is converted to the unit measured in the test apparatus (mol H_2 s^{-1} kg^{-1}) through division by 5.765 kg, the mass of DEB required to absorb 62.2 moles of hydrogen. This figure is further divided by a factor of two, to account for the second programmatic requirement. The result is 1.0×10^{-6} mol H_2 s^{-1} kg^{-1}. Getter performance is compared to this figure in the rest of this report.

Tests to evaluate operating temperature range and poison effects in an atmosphere of 5% H_2 in N_2 were performed on all materials (6 getters consisting of various coatings on DEB plus uncoated DEB as a control, Table 5 in Section 3.3). In conjunction with information on process knowledge and material costs, results from these tests were used to select 2 coated getters (polystyrene-coated DEB and polybenzylmethacrylate-coated DEB) for additional testing. Uncoated DEB was also the subject of continued testing as a control measure. A phased test strategy was needed to focus testing on a manageable number of materials, consistent with schedule and funding constraints.

Two types of data plots for getter materials are presented: 1) plots of hydrogen removal rate versus reciprocal temperature and 2) histograms comparing rates under a range of test conditions other than temperature. All hydrogen removal rates are calculated relative to the theoretical hydrogen capacity of

DEB. This methodology provides a uniform datum from which to compare empirically measured variations in DEB capacity.

The following are sources of uncertainty in the dynamic tests:

1. Weighing of materials (±0.0005 grams)

2. Gas composition (±2%)

3. Gas flow rate (+2%)

4. Measurement of hydrogen (±0.13)

5. Stoichiometric variation

    a. Within the same lot of DEB due to sample size heterogeneity

    b. Between lots of DEB

Error analysis of these uncertainties (excluding stoichiometric variation) produces a total uncertainty of ±33% for hydrogen removal rates at 50% saturation. To assess uncertainties from stoichiometric variation due to the size of the sample used within rate measurement tests (0.10 to 0.25 grams), rate measurements were performed on replicate samples from three DEB stocks (lot x170, lot x245, and lot x222) (Table 6 and Figure 15). Three rate measurements performed on lots x245 and x222 produced results within 2% and 19%, respectively. Of three rate measurements performed on lot x170, two were within the 15% but a third was within 50%. Uncertainties due to stoichiometric variation and compositional heterogeneity are discussed below.

Table 6. Replicate samples and variability of hydrogen removal rate (mole H_2 s^{-1} kg^{-1} at 50% capacity) in DEB lots x170, x245, and x222 in an atmosphere of 5% H_2 in nitrogen at a temperature of 77ºF (25ºC). Minimum programmatic criteria is 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}.

Uncoated DEB	Replicate Tests				Mean
Lot x170	2.34E-04	1.45E-04	2.74E-04		2.18±0.66E-04
Lot x245	6.84E-04	7.00E-04	6.89E-04		6.91±0.08E-04
Lot x222	6.31E-04	5.31E-04	5.43E-04	5.88E-04	5.73±0.46E-04

4.2.1 Capacity of Getter Materials

Capacity measurements were performed on uncoated DEB lot x170 and lot x245. The results are plotted in Figure 16. The theoretical capacity of DEB, 10.8 moles hydrogen per kilogram (mol H_2 kg^{-1}), is also plotted. The empirically measured capacity for lot x170, 9.1 mol H_2 kg^{-1}, is approximately 15% less than the theoretical capacity. In contrast, the empirically measured capacity for lot x245, 18.5±0.68 mol H_2 kg^1, is approximately 72% greater than the theoretical capacity. The variation in empirical capacity may represent the actual stoichiometric variation between different lots of DEB, as suggested by the variation in hydrogen removal rates depicted in Figure 15.
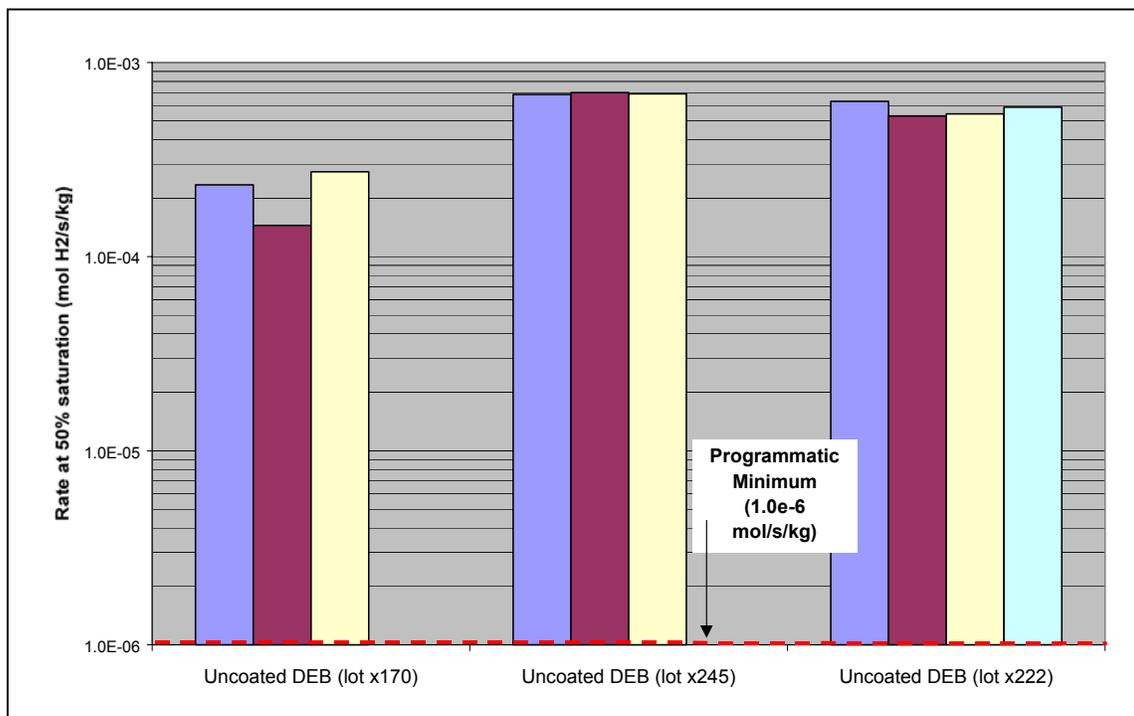
Figure 15. Replicate samples and variability of hydrogen removal rate in DEB (mole H_2 s^{-1} kg^{-1} at 50% of capacity) lots x170, x245, and x222 in an atmosphere of 5% H_2 in nitrogen at a temperature of 77ºF.
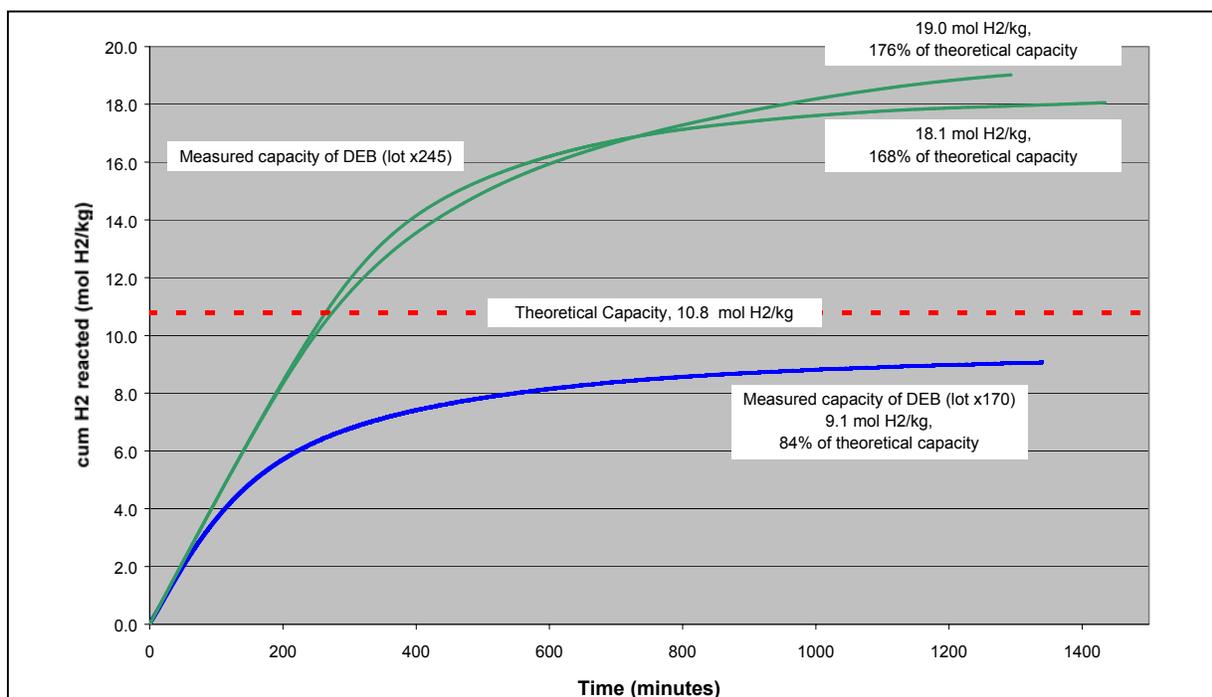
Figure 16. Hydrogen capacity measured for DEB lots x170 and x245 in an atmosphere of 5% H_2 in nitrogen at a temperature of 77ºF (25ºC). Two replicate tests are shown for DEB lot x245.

Emperically measured capacities for polystyrene- (16.4 mol H_2 kg^{-1}) and polybenzylmethacrylate- (16.1 mol H_2 kg^{-1}) coated DEB (lot x245) are approximately 10% less than the capacity measured for uncoated DEB. The coatings are a very small fraction of the total mass of getter material, much less than 1% (by weight). Therefore, it is not known why coated DEB yields a smaller capacity compared to uncoated DEB. However, this relationship may be due to the slower hydrogen removal rates of the coated materials and the finite time of the capacity measurements. The slightly reduced capacity measured for coated DEB is consistent with the capacities measured by SRTC using an alternate method, as discussed later in this report.

The apparent variation in hydrogen capacity between DEB lots x170 and x245 (Figure 16) is smaller than the variation in hydrogen removal rate (at 50% saturation) measured for these lots (Figure 15). This difference is due to the method of calculating rate based on theoretical capacity. Rates that are calculated from empirically measured capacities (Table 5) produce results that are consistent with the empirically measured variation in hydrogen capacity. It should be noted that the difference in the removal rate that is based on theoretical capacity and the rate that is based on empirical capacity is within the uncertainty of the dynamic test method.

Table 7. Comparison of Hydrogen Removal Rate relative to Theoretical and Empirical Hydrogen Capacity of DEB.   Note that these data are reported for one test and do not reflect mean rates based on replicated tests reported elsewhere in this report.

	Rate (mol H_2 s^{-1} kg^{-1}) at 50 % Saturation		
	Based on Theoretical Capacity	Based on Empirical Capacity	Relative Difference
DEB lot x170	2.74E-04	3.73E-04	+36%
DEB lot x245	7.00E-04	6.38E-04	-9%

4.2.2   Operating Temperature Range

Temperatures required by the Test Plan to evaluate the operating temperature range of getter materials are 160, 77, 23, and –20ºF (71.1, 25, -5, and -28.9ºC). Additional tests were performed at 122°F (50ºC) in an atmosphere of hydrogen in nitrogen. Additional tests at 122ºF (50°C) were performed to evaluate getter behavior at a temperature midway between ambient temperature and the hottest temperatures expected in the TRUPACT-II.

4.2.2.1   Hydrogen in Nitrogen

Rate measurements were performed on all materials (Table 5 in Section 3.3) in an atmosphere of 5% H_2 in N_2 over the temperature range of 160 to 77ºF (71.1 to 25ºC). Test results are summarized in Table 8 and presented in Figure 17. In general, uncoated DEB exhibits the largest rate of hydrogen removal relative to the various coated DEB materials. However, all materials exhibit hydrogen removal rates that exceed the programmatic minimum for this temperature range. Hydrogen removal rates exceed the programmatic minimum by 1.5 to 2.5 orders of magnitude in these tests.

Table 8. Hydrogen removal rate (mole H_2 s^{-1} kg^{-1} at 50% capacity) for hydrogen getters in an atmosphere of 5% H_2 in nitrogen at temperatures of 160 to 23ºF (71.1 to -5ºC). Removal rates are also reported for uncoated DEB (lot x170), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB at a temperature of -20ºF (–28.9ºC). Minimum programmatic criteria is 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}.

T (F)	T (C)	T (K)	1000/T (K)	Uncoated DEB (lot x170)	Polystrene	Polystyrene-co-methylmethacrylate	Polyiospropyl methacrylate	Polybenzyl methacrylate	Kynar (PVDF)	CMS-3	CMS-3 packet
160	71.1	344	2.90	6.06E-04	2.81E-04	1.13E-04	3.48E-04	1.16E-04	2.00E-04	6.50E-04	3.00E-04
122	50	323	3.09	6.72E-04	5.22E-04	3.07E-04	1.31E-04	8.81E-05	5.56E-05	6.86E-04	2.78E-04
77	25	298	3.35	2.18E-04	3.83E-04	1.90E-04	9.05E-05	2.36E-04	1.16E-04	6.07E-04	2.27E-04
23	-5	268	3.73	1.41E-04	7.36E-05	1.84E-04		6.21E-05	1.63E-04	1.28E-04	
-20	-28.9	244	4.09	1.25E-04	1.75E-05			1.24E-05			
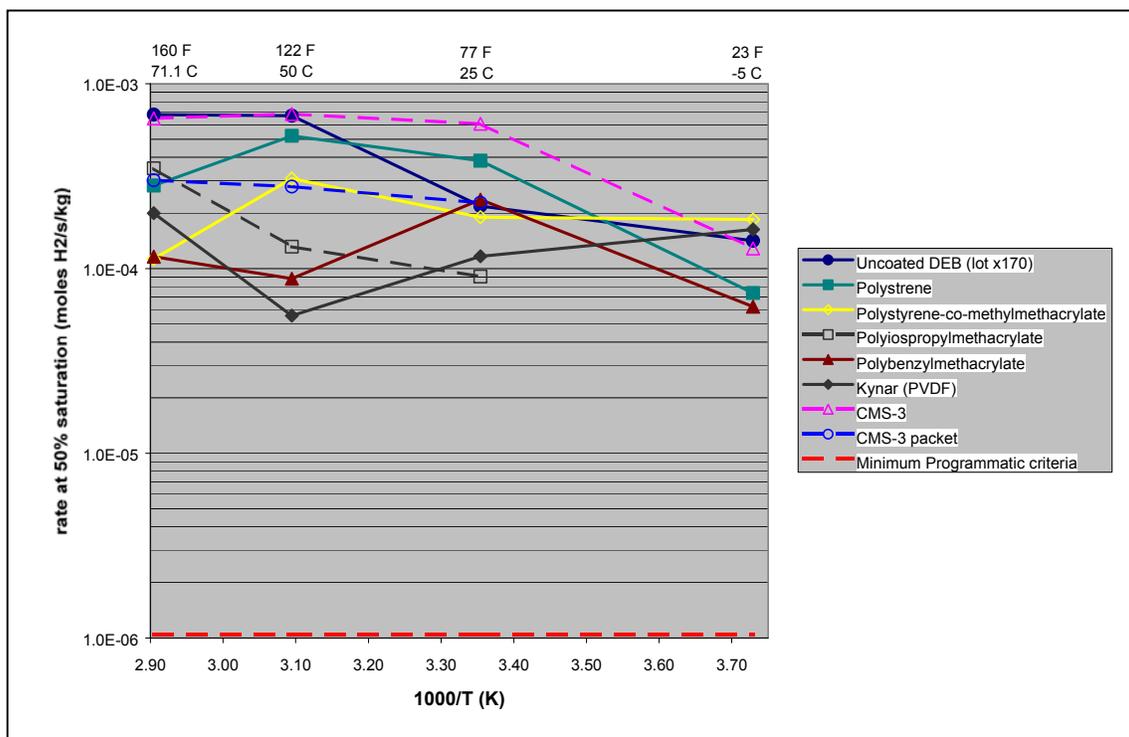
Figure 17. Plot of hydrogen removal rate vs. temperature (reciprocal Kelvin multiplied by 1000) for hydrogen getters in an atmosphere of 5% H_2 in nitrogen at temperatures of 160 to 23ºF (71.1 to -5ºC).

Results from tests performed in nitrogen for the limited temperature range (160 to 23ºF, 71.1 to -5ºC) were used to select 2 coated getters (polystyrene-coated DEB and polybenzylmethacrylate-coated DEB) for additional testing. Uncoated DEB was also the subject of continued testing as a control measure. Additional rate measurements were performed on uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 5% H_2 in N_2 at -20ºF (-28.9ºC). Test results for these three materials are summarized in Table 8 and presented as Arrhenius plots (Figure 18) for the full temperature interval (160 to -20ºF, 71.1 to –28.9ºC) specified in the Test Plan. All three materials exhibit hydrogen removal rates that exceed the programmatic minimum for this temperature range. At -20ºF (-28.9ºC), hydrogen removal rates exceed the programmatic minimum by approximately 1 (polystyrene-coated DEB and polybenzylmethacrylate-coated DEB) to 2 (uncoated DEB) orders of magnitude.

Uncoated DEB and polystyrene-coated DEB exhibit Arrhenius behavior over the temperature range of 122 to -20ºF (50 to –28.9ºC). Arrhenius behavior is exhibited by polybenzylmethacrylate-coated DEB over a narrower temperature interval of 77 to -20ºF (25 to –28.9ºC). A slope change of the Arrhenius plots occurs at temperatures greater than 122ºF (50ºC) for uncoated DEB and polystyrene-coated DEB and at a temperature greater than 77ºF (25ºC) for polybenzylmethacrylate-coated DEB. Non-Arrhenius behavior indicates a change in reaction mechanism, either due to a change in the actual chemical reaction that is taking place or to other physical or chemical influences. Materials recovered from tests performed at 160ºF (71.1ºC) exhibited physical changes, including adhesion of individual grains as sticky masses and plugs. Similar changes were observed in 122ºF (50ºC) tests with uncoated DEB and polystyrene-coated DEB. Polybenzylmethacrylate-coated DEB did not exhibit these changes in tests performed below 160ºF (71.1ºC). The general correlation between change in physical state of the materials and decrease in slope at higher temperature suggests that the two phenomena are related. However, despite these phenomena, hydrogen removal rates at elevated temperature exceed the programmatic minimum by approximately 2 to 2.5 orders of magnitude.
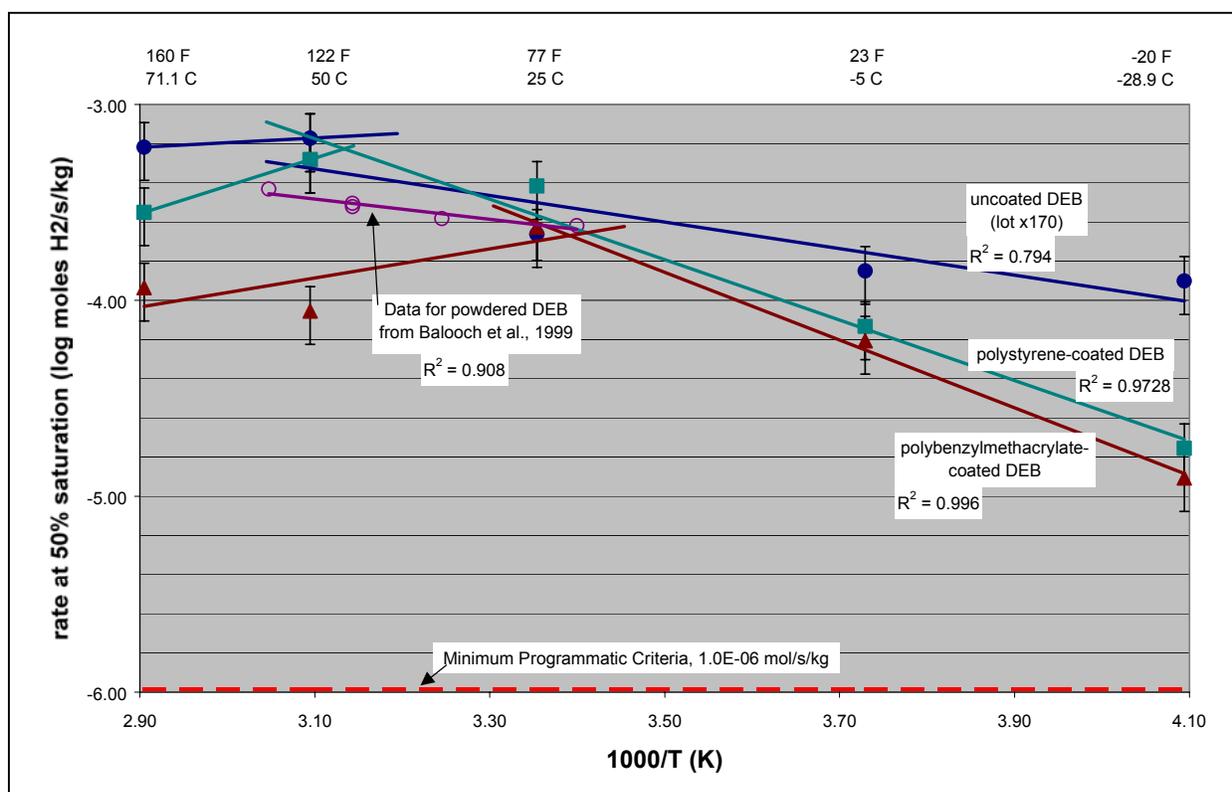
Figure 18. Arrhenius plot (hydrogen removal rate vs. temperature) for uncoated DEB (lot x170), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 5% H_2 in nitrogen at temperatures of 160 to -20ºF (71.1 to –28.9ºC). The hydrogen removal rate is plotted as log mole H_2 s^{-1} kg^{-1} at 50% capacity and the temperature is plotted as reciprocal Kelvin multiplied by 1000. Error bars represent maximum uncertainty. Plotted for comparison are data for powdered DEB reported by Balooch *et al*., 1999 for the temperature range of 21 to 55ºC.

Little has been published on the kinetics of DEB hydrogenation. Balooch *et al*. (1999) evaluated the hydrogenation kinetics of DEB at four temperatures, 21°C, 35°C, 45°C and 55°C. Their data set is reproduced in Figure 18 and agrees reasonably well with the kinetic data determined in this study for

24

uncoated DEB. Balooch *et al*. (2001) examined the hydrogenation kinetics of DEB imbedded in silicone (40% DEB getter mixture and about 60% silicone by weight). They concluded that the hydrogenation kinetics of the DEB-silicone mix is mainly controlled by the diffusion of hydrogen in the silicone matrix. The results of Balooch *et al*. (2001) are not directly comparable to our work because the polymer coatings that we used comprise a much smaller proportion of the total mass in contrast to the DEB-silicone mix.

4.2.2.2 *Hydrogen in Air*

Additional rate measurements were performed on uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 3% H_2 in air for the temperature range of 160 to -20ºF (71.1 to –28.9ºC). Test results for these three materials are summarized in Table 9 and presented as Arrhenius plots (Figure 19). All three materials exceed the programmatic minimum by approximately 2 to 2.5 orders of magnitude for this temperature range. The effect of carbon monoxide (0.5%) is quite pronounced, reducing the coated and uncoated DEB performance by approximately one order-of-magnitude. This fall off in performance is most striking for the uncoated DEB, where the rate is reported for a saturation of 28% because reliable tests could not be performed to the 50% saturation level. The rate at 50% could not be projected from the existing data set, but is presumed to be less than the rate reported for 28% (2.04E-05 mol H_2 s^{-1} kg^{-1}).

Table 9. Hydrogen removal rate (mole H_2 s^{-1} kg^{-1} at 50% capacity) for uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 3% H_2 in air at temperatures of 160 to -20ºF (71.1 to –28.9ºC). Minimum programmatic criteria is 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}.

T (F)	T (C)	T (K)	1000/T (K)	Uncoated DEB (lot x170)	Uncoated DEB (lot x245)	Polystrene	Polybenzylmethacrylate
160	71.1	344	2.90	6.82E-04	7.34E-04	4.62E-04	4.68E-04
77	25	298	3.35	5.51E-04	6.53E-04	3.81E-04	3.37E-04
23	-5	268	3.73		5.79E-04	1.73E-04	1.39E-04
-20	-28.9	244	4.09		5.17E-04	2.49E-04	3.59E-04

In contrast to rates measured in an atmosphere of nitrogen, uncoated DEB exhibits Arrhenius behavior over the entire temperature range that was tested. Polystyrene-coated DEB and polybenzylmethacrylate-coated DEB also exhibit Arrhenius behavior across the entire temperature range, with the exception of an anomaly at 23ºF (-5ºC). The cause of this anomaly is uncertain, but it may be the result of proximity to the freezing point of water.

25
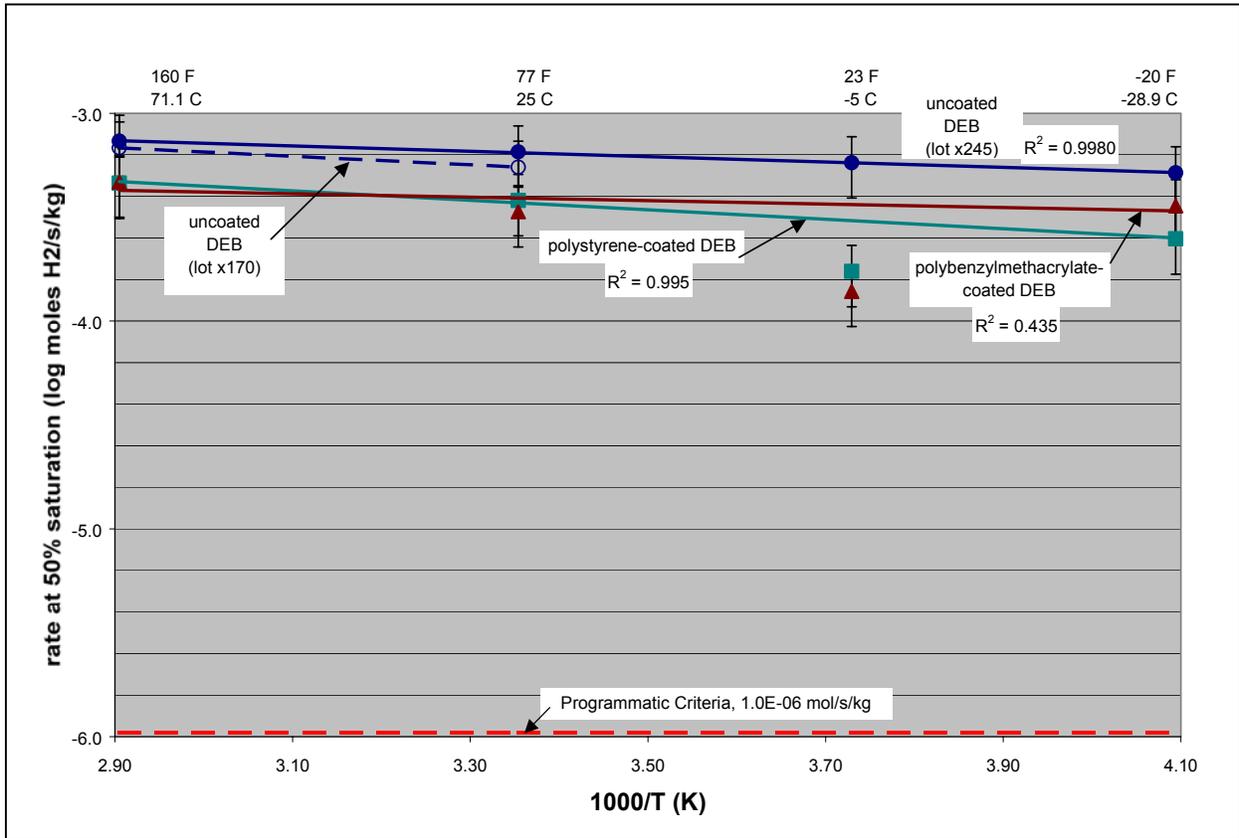
Figure 19. Arrhenius plot (hydrogen removal rate vs. temperature) for uncoated DEB (lots x170 and x245), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 3% H_2 in air at temperatures of 160 to -20ºF (71.1 to –28.9ºC). The hydrogen removal rate is plotted as log mole H_2 s^{-1} kg^{-1} at 50% capacity and the temperature is plotted as reciprocal Kelvin multiplied by 1000. Trend lines connect rate data at all temperatures except 23ºF (-5ºC). Error bars represent maximum uncertainty.

Hydrogen removal rates for uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB are greater in air compared to nitrogen because of the catalytic recombination reaction to form water. The difference between hydrogen removal rates measured in nitrogen and air is more pronounced at lower temperature, producing an Arrhenius plot for rates in air that is flatter than the plot for rates in nitrogen. The reason for the greater rate difference at lower temperature is uncertain, but may be due to the effect of the recombination reaction and the formation of ice.

4.2.3 Effect of Hydrogen Concentration

Rate measurements at two hydrogen concentrations were made to determine how rates of hydrogen removal are affected by hydrogen concentration. Measurements were performed on uncoated DEB (lot x170 and x245), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 1% H_2 in N_2 at the temperature of 77ºF (25ºC). Test results comparing rates in 1 and 5% H_2 are presented in a histogram (Figure 20). Removal rates do not exhibit significant change between the two gas compositions for uncoated DEB lot x170, and polybenzylmethacrylate-coated DEB. The removal rate for uncoated DEB lot x245 exhibits a measurable rate decrease of approximately 50% for 1% hydrogen relative to 5% hydrogen. The removal rate for polystyrene-coated DEB also exhibits a measurable rate decrease of approximately 37%. Based on these results, we conclude that hydrogen absorption rate is not affected by changes in hydrogen concentration for two of the four materials, and minimally diminished for the other two.
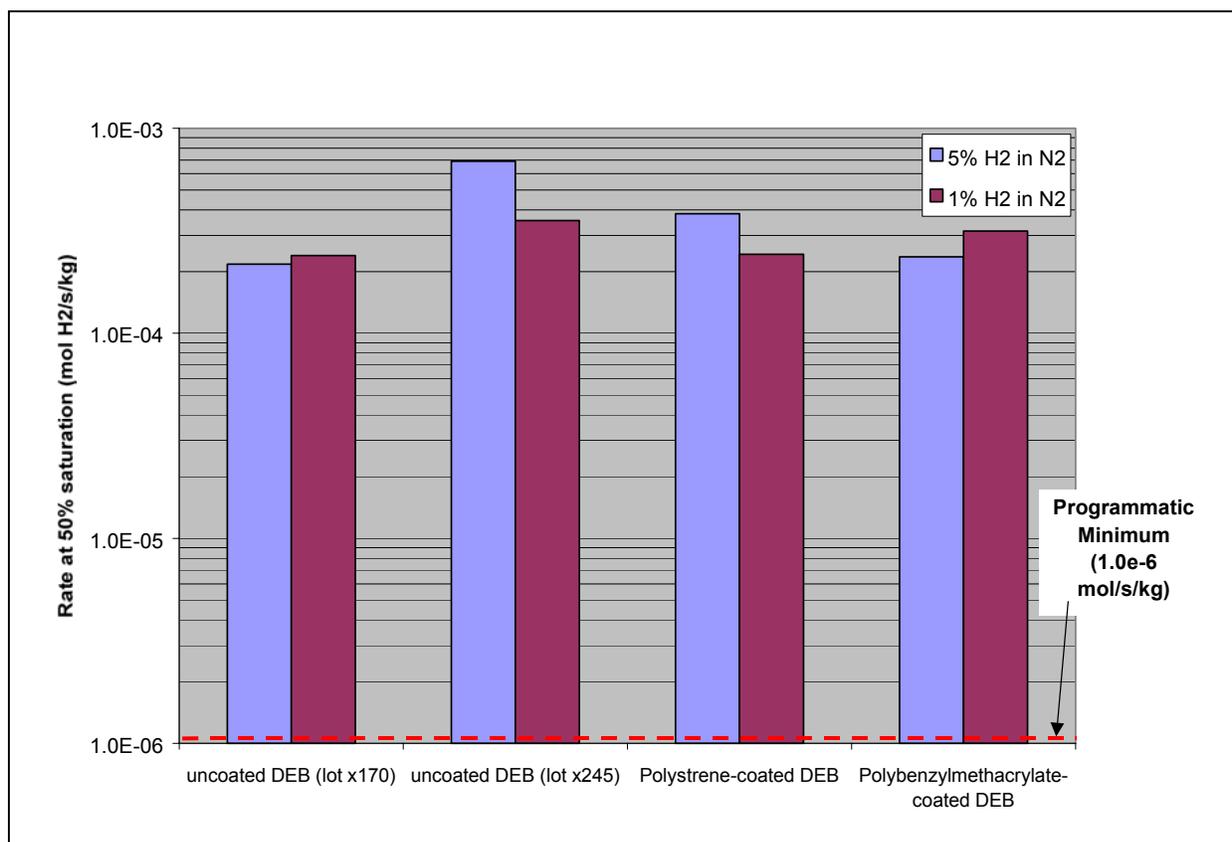
Figure 20. Comparison of hydrogen removal rates in uncoated DEB (lot x170 and x245), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 1 and 5% H_2 in nitrogen at a temperature of 77ºF (25ºC).

4.2.4 Poison Effects

The compounds selected for screening as potential poisons are listed in Table 10. The poison-screening tests were conducted in the presence of an excess of poison vapor. An organic vapor concentration of approximately 1000 part per million (ppm) was used. In the case of carbon monoxide, a gas concentration of approximately 1% was used.

Table 10. Poisons for Getter Screening

Represented Class	Selected Compound(s)
Aliphatic	Hexane
Aromatic	Toluene
Ketone	Acetone
Alcohol	Methanol
Chlorinated organic	Carbon tetrachloride
Inorganic gases	Carbon monoxide

4.2.4.1 Hydrogen in Nitrogen

Rate measurements were performed on all materials (Table 5 in Section 3.3) in an atmosphere of 5% H_2 in N_2 at a temperature of 77ºF (25ºC) in the presence of the poisons listed in Table 10. The effect of poisons on hydrogen removal rate at 77ºF (25ºC) is summarized in Table 11 and plotted in Figure 21. Poisons impact the hydrogen removal rate of all of the materials at 77ºF (25ºC). However, all materials exhibit removal rates that exceed the programmatic minimum by at least 1 order of magnitude.

At 77ºF (25ºC), toluene actually enhances hydrogen removal rates for all materials that were tested (Table 11 and Figure 21). Hexane enhances removal rates for all coated DEB tested. The cause of this enhancement is unknown. Acetone and methanol impact the various coatings differently, enhancing the removal rates of some materials (*e.g.* kynar-coated DEB), reducing rates for other materials (*e.g.* polystyrene-coated DEB), and having no measurable effect on others (*e.g.* acetone with polybenzylmethacrylate-coated DEB). The causes for these impacts are unknown. Carbon tetrachloride and carbon monoxide provide the greatest impact. Carbon tetrachloride reduces hydrogen removal rates for all materials except polystyrene-co-methylmethacrylate- and Kynar-coated DEB. These two materials appear to mitigate the effect of carbon tetrachloride. Carbon tetrachloride reduces rates for uncoated DEB by approximately 0.5 orders of magnitude. All of the coatings reduce the impact of carbon tetrachloride by a factor of two or more. Carbon monoxide reduces the removal rate for uncoated DEB and polybenzylmethacrylate-coated DEB by approximately one order of magnitude.

Rate measurements were performed on all materials (Table 5 in Section 3.3) in an atmosphere of 5% H_2 in N_2 at a temperature of 160ºF (71.1ºC) in the presence of carbon tetrachloride. The effect of carbon tetrachloride at 160ºF (71.1ºC) is summarized in Table 12 and plotted in Figure 22. Carbon tetrachloride does not measurably impact hydrogen removal rates in uncoated DEB or in polystyrene-co-methylmethacrylate-, Polyiospropylmethacrylate-, and CMS-3 coated DEB. Hydrogen removal rates in polystyrene-coated DEB and PVDF-coated DEB appear to be slightly enhanced whereas the removal rate in polybenzylmethacrylate-coated DEB appears to be slightly diminished. However, at 160ºF (71.1ºC), all materials exhibit removal rates that exceed the programmatic minimum in the presence of carbon tetrachloride by at least 1 order of magnitude.

Table 11. Effect of poisons on hydrogen removal rates (mole H$_2$ s-1 kg-1) of DEB and coated DEB at 77ºF (25ºC) in an atmosphere of 5% hydrogen in nitrogen. The minimum programmatic criteria is 1.0 x 10-6 mol H$_2$ s-1 kg-1.

Material	no poison	hexane	toluene	acetone	methanol	carbon tetrachloride	carbon monoxide
Uncoated DEB (x170)	2.18E-04			8.26E-05			
Uncoated DEB (x245)	6.91E-04	6.63E-04	1.11E-03		9.30E-04	1.89E-04	6.47E-05
Polystrene	3.83E-04	5.90E-04	5.07E-04	1.93E-04	9.45E-05	1.37E-04	4.44E-05
Polystyrene-co-methylmethacrylate	1.90E-04	5.34E-04	4.14E-04	2.33E-04	2.16E-04	1.37E-04	
Polyisopropylmethacrylate	9.05E-05	1.86E-04	2.02E-04	6.36E-05	2.22E-04	4.16E-05	
Polybenzylmethacrylate	2.36E-04	4.16E-04	3.52E-04	2.21E-04	1.09E-04	1.11E-04	2.63E-05
Kynar (PVDF)	1.16E-04	2.79E-04	9.02E-04	1.91E-04	3.31E-04	1.38E-04	
CMS-3	6.07E-04			9.68E-04	6.90E-04	1.93E-04	
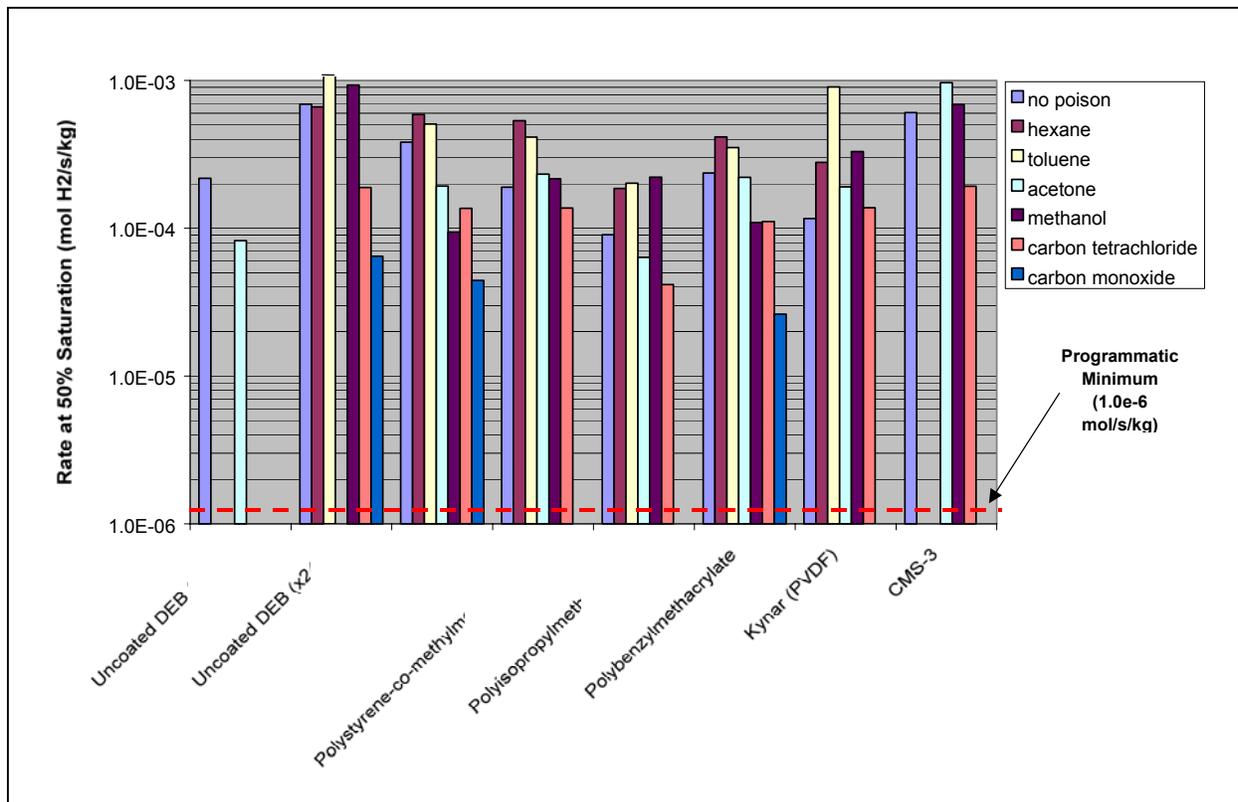
Figure 21. Effect of poisons on hydrogen getter rates in an atmosphere of 5% H$_2$ in nitrogen at a temperature of 77ºF (25ºC).

Table 12. Effect of carbon tetrachloride on hydrogen removal rates (mole H_2 s-1 kg-1) of DEB and coated DEB at 160ºF (71.1ºC) in an atmosphere of 5% hydrogen in nitrogen. The minimum programmatic criteria is 1.0 x 10-6 mol H_2 s-1 kg-1.

Material	no poison	carbon tetrachloride
Uncoated DEB (x170)	6.81E-04	4.42E-04
Polystrene	2.81E-04	4.28E-04
Polystyrene-co-methylmethacrylate	1.13E-04	9.52E-05
Polyisopropylmethacrylate	3.48E-04	2.82E-04
Polybenzylmethacrylate	1.16E-04	4.24E-05
Kynar (PVDF)	2.00E-04	2.71E-04
CMS-3	6.50E-04	6.27E-04
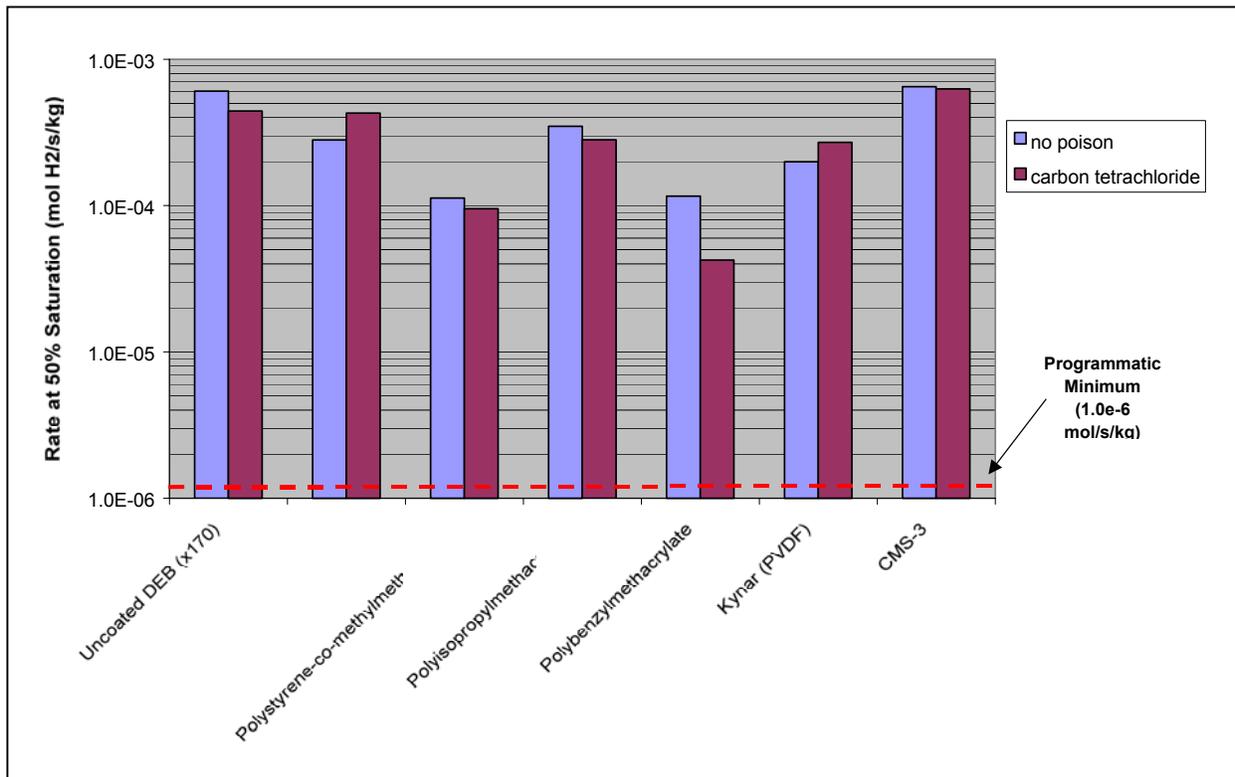
Figure 22. Effect of carbon tetrachloride on hydrogen getter rates in an atmosphere of 5% H_2 in nitrogen at a temperature of 160ºF (71.1ºC).

These test results, in conjunction with data collected to evaluate operating temperature range, were used to select 2 coated getters (polystyrene-coated DEB and polybenzylmethacrylate-coated DEB) for additional testing, as described in the following section. Uncoated DEB was also the subject of continued testing as a control measure. A comparison of hydrogen removal rates for these three materials in the presence and absence of 1,000 ppm carbon tetrachloride is presented in Table 13. The following may be concluded from these data:

1. Hydrogen removal rates are greatest in uncoated DEB and progressively decrease in polystyrene- and polybenzylmethacrylate-coated DEB, respectively.

2. In comparing the hydrogen removal rate in an inert atmosphere versus an atmosphere containing carbon tetrachloride, the largest rate decrease is displayed by uncoated DEB. Rates for polystyrene- and polybenzylmethacrylate-coated DEB exhibit less of an effect from carbon tetrachloride, in that order.

3. The hydrogen removal rate in an atmosphere of carbon tetrachloride is approximately the same for all three materials.

It is of note that these results (Table 13) are consistent with the permeability data presented in Table 4 of Section 3.1. The data presented in Table 4 were generated with a pressure differential of 20 psi in an atmosphere of 1,000 ppm carbon tetrachloride. In contrast, the dynamic test apparatus used for Phase 2 employed no pressure differential.

Table 13. Comparison of hydrogen removal rates (mole H_2 s^{-1} kg^{-1}) in the presence and absence of 1,000 ppm carbon tetrachloride. Temperature is 77ºF (25ºC) and the atmosphere is 5% hydrogen in nitrogen. Minimum programmatic criteria is 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}.

Material	no poison	carbon tetrachloride	Rate ratio: CCl_4/no poison	Rate ratio: no poison/CCl_4
Uncoated DEB (x245)	6.91E-04	1.89E-04	0.27	3.66
Polystrene	3.83E-04	1.37E-04	0.36	2.80
Polybenzylmethacrylate	2.36E-04	1.11E-04	0.47	2.12

4.2.4.2   Hydrogen in Air

Rate measurements were performed on uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 3% H_2 in air at a temperature of 77ºF (25ºC) in the presence of the organic poisons listed in Table 10. The results are summarized in Table 14 and plotted in Figure 23. Toluene, acetone, and methanol actually enhance removal rates for all materials with one exception. The apparent increase in rate exhibited by polystyrene-coated DEB in the presence of methanol is at the upper limit of uncertainty. Hexane does not effect the removal rates for uncoated DEB and enhances removal rates for polystyrene-coated DEB and polybenzylmethacrylate-coated DEB. The cause of this enhancement is unknown. Carbon tetrachloride does not effect the removal rate for uncoated DEB and polystyrene-coated DEB (within the limits of uncertainty). Carbon tetrachloride slightly diminishes the removal rate for polybenzylmethacrylate-coated DEB. The effect of carbon tetrachloride on removal rates of hydrogen in air is less pronounced than the effect on removal rates of hydrogen in nitrogen. At 77ºF (25ºC), all three materials exhibit removal rates that exceed the programmatic minimum by approximately 2 orders of magnitude.

Table 14. Effect of poisons on hydrogen removal rates (mole H_2 s-1 kg-1) of uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB at 77ºF (25ºC) in an atmosphere of 3% hydrogen in air. The hydrogen removal rate is reported for 50% capacity except for uncoated DEB with carbon monoxide (rate reported for 28% saturation) and polystyrene-coated DEB with carbon monoxide (rate reported for 43% saturation). The minimum programmatic criteria is 1.0 x 10-6 mol H_2 s-1 kg-1.

Material	no poison	hexane	toluene	acetone	methanol	carbon tetrachloride	Carbon monoxide (0.5%)
Uncoated DEB (x245)	6.53E-04	6.74E-04	1.33E-03	1.20E-03	1.07E-03	6.53E-04	2.04E-05
Polystrene	3.81E-04	6.57E-04	9.82E-04	6.77E-04	5.08E-04	2.61E-04	1.32E-05
Polybenzylmethacrylate	3.37E-04	6.96E-04	5.65E-04	1.13E-03	9.87E-04	2.07E-04	2.67E-05
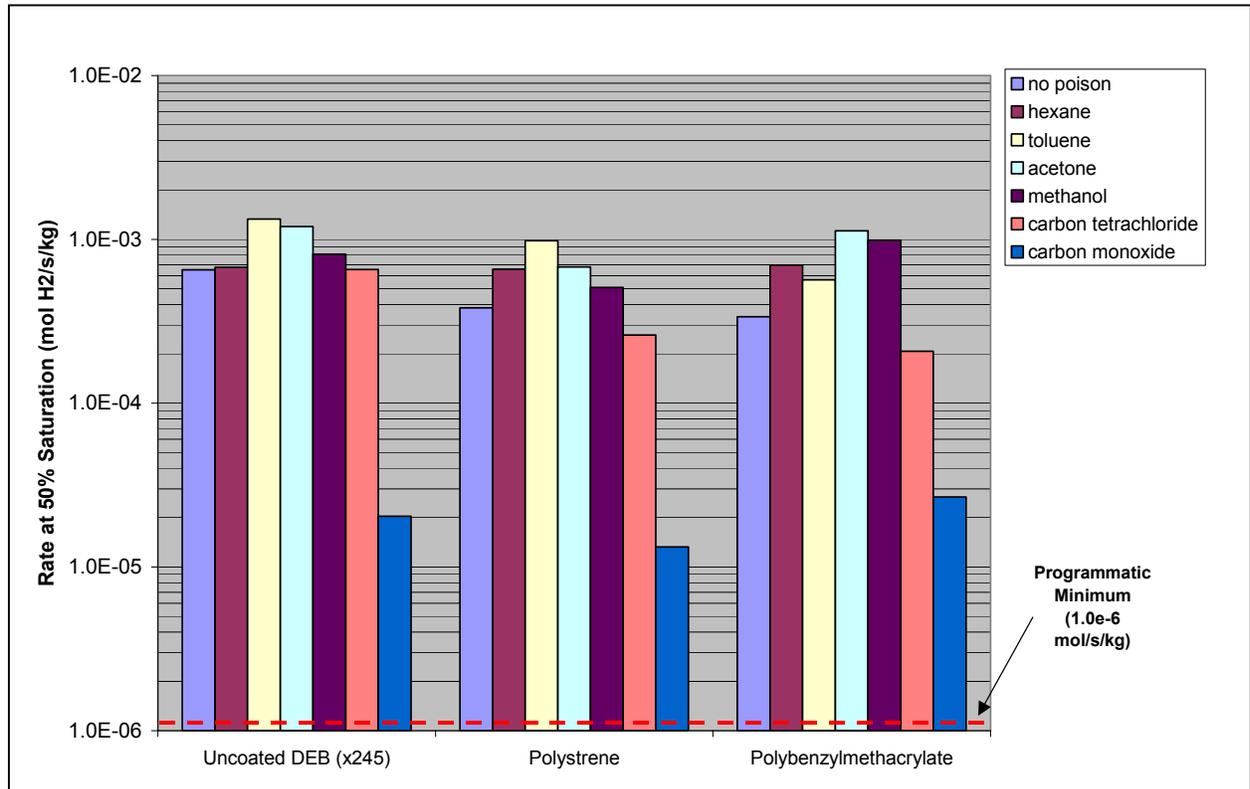
Figure 23. Effect of poisons on uncoated DEB (lot x245), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB getter rates in an atmosphere of 3% H_2 in air at a temperature of 77ºF (25ºC). The hydrogen removal rate is plotted as mole H_2 s^{-1} kg^{-1} at 50% capacity except for uncoated DEB with carbon monoxide (rate reported for 28% saturation) and polystyrene-coated DEB with carbon monoxide (rate reported for 43% saturation).

Rate measurements were performed on uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 3% H_2 in air at a temperature of 160ºF (71.1ºC) in the presence of carbon tetrachloride. The effect of carbon tetrachloride at 160ºF (71.1ºC) is summarized in Table 15 and plotted in Figure 24. Carbon tetrachloride does not exhibit a measurable effect on removal rates for hydrogen in air at 160ºF (71.1ºC).

Table 15. Effect of carbon tetrachloride on hydrogen removal rates (mole H_2 s-1 kg-1) of uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB at 160ºF (77.1ºC) in an atmosphere of 3% hydrogen in air. The minimum programmatic criteria is 1.0 x 10-6 mol H_2 s-1 kg-1.

Material	no poison	carbon tetrachloride
Uncoated DEB (x245)	7.34E-04	6.85E-04
Polystrene	4.62E-04	4.76E-04
Polybenzylmethacrylate	4.68E-04	5.68E-04
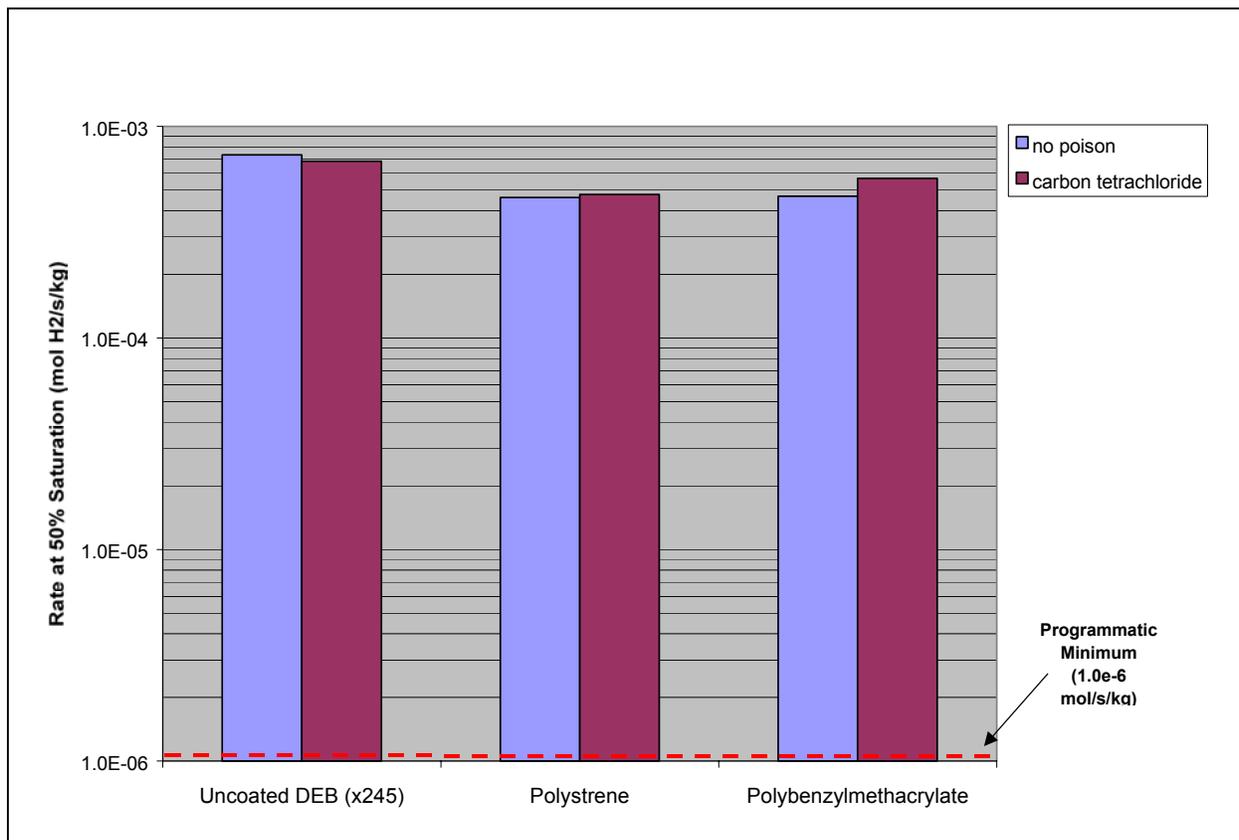
Figure 24. Effect of carbon tetrachloride on uncoated DEB (lot x245), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB getter rates in an atmosphere of 3% H_2 in air at a temperature of 160ºF (71.1ºC).

4.2.4.3   Synergy of Poisons

Tests were performed on uncoated DEB (lot x245), polystyrene-, and polybenzylmethacrylate-coated DEB to evaluate the impact on hydrogen removal rate of a mixture of poisons known to inhibit getter performance. A carbon tetrachloride concentration of approximately 1000 ppm mixed with a carbon monoxide concentration of approximately 1% in an atmosphere of 5% H_2 in nitrogen was used in testing. The results are summarized in Table 16 and plotted in Figure 25. The combination of the two poisons impact the hydrogen removal rate of all of the materials that were tested. Rates in uncoated DEB and polystyrene-coated DEB are reduced by approximately one order-of-magnitude. The rate observed for polybenzylmethacrylate-coated DEB is reduced by approximately 70%. However, despite these impacts, all three materials exhibit removal rates that exceed the programmatic minimum by at least one order-of-magnitude.

Table 16. Effect of carbon tetrachloride (1000 ppm) plus carbon monoxide (1%) on hydrogen removal rates (mole H_2 s^{-1} kg^{-1}) of uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB at 77ºF (25ºC) in an atmosphere of 5% hydrogen in nitrogen. Minimum programmatic criteria is 1.0×10^{-6} mol H_2 s^{-1} kg^{-1}.

Material	no poison	carbon tetrachloride + carbon monoxide
Uncoated DEB (x245)	6.91E-04	8.91E-05
Polystrene	3.83E-04	1.14E-05
Polybenzylmethacrylate	2.36E-04	8.03E-05
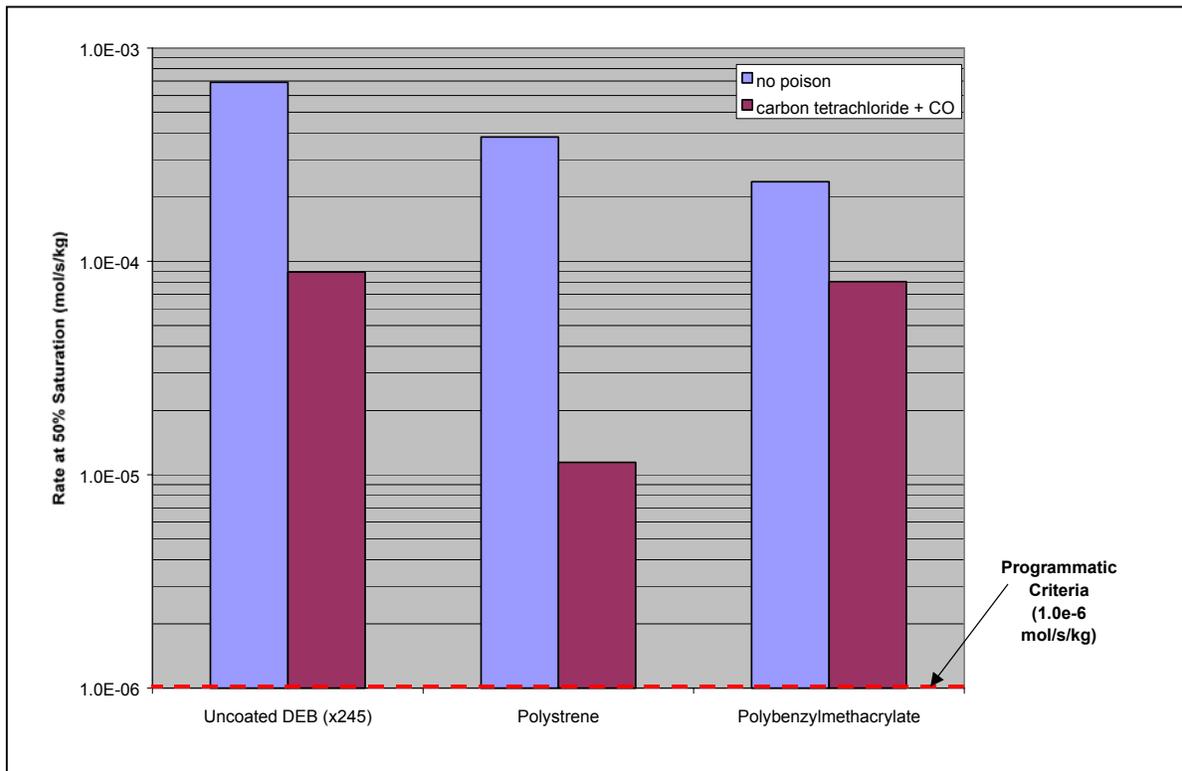
Figure 25. Effect of carbon tetrachloride (1000 ppm) plus carbon monoxide (1%) on hydrogen removal rates (mole H_2 s^{-1} kg^{-1} at 50% capacity) of uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB at 77ºF (25ºC) in an atmosphere of 5% hydrogen in nitrogen.

4.2.4.4   Free Liquids

The getter material will be operated in air—potentially resulting in formation of water vapor—up to the scaled loading for use in the TRUPACT-II. The total maximum quantity of water that could produced by recombination of hydrogen with oxygen is calculated from the maximum level of hydrogen production that has been determined by the program (1.2×10^{-5} mol H_2 s^{-1}) and the maximum amount of time specified for containment in the TRUPACT-II (60 days). The result is 62 moles, or 1.1 liters of liquid water. This value is significantly below the limited mandated for the TRUPACT-II payload.

Tests were performed on uncoated DEB (lot x245), polystyrene-, and polybenzylmethacrylate-coated DEB to evaluate the impact of water vapor on hydrogen removal rate. The tests were conducted at 77ºF (25ºC) in an atmosphere of 5% hydrogen in nitrogen that contained approximately 20,000 ppm H_2O (relative humidity of 67%). The hydrogen removal rate was measured at low getter capacity (approximately 5%) and at approximately 50% getter capacity to determine the impact of water formation. The results are summarized in Table 17. In the presence of water vapor, the hydrogen removal rate of uncoated DEB remained unchanged between 5% and 50% capacity. Rates decreased slightly for polystyrene- and polybenzylmethacrylate-coated DEB. Compared to tests conducted without water vapor, the hydrogen removal rate at 50% capacity of uncoated DEB and polystyrene-coated DEB increased by a factor of approximately two. The hydrogen removal rate of polybenzylmethacrylate-coated DEB was not affected by water vapor.

Table 17. Effect of water vapor (20,000 ppm, relative humidity of 67%) on hydrogen removal rates (mole H_2 s^{-1} kg^{-1}) of uncoated DEB, polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB at 77ºF (25ºC) in an atmosphere of 5% hydrogen in nitrogen. Minimum programmatic criteria is 1.0×10^{-6} mol H_2 s^{-1} kg^{-1}.

	water vapor present		no water vapor
Material	5% DEB saturation	50% DEB saturation	50% DEB saturation
Uncoated DEB (x245)	1.45E-03	1.43E-03	6.91E-04
Polystrene	1.00E-03	8.14E-04	3.83E-04
Polybenzylmethacrylate	2.53E-04	1.50E-04	2.36E-04

4.2.5   Effect of Aging

Tests were performed on "aged" samples of uncoated DEB (lots x170 and x245), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB to evaluate the impact of long-term storage at elevated temperature on getter performance. These "aged" samples were evaluated for hydrogen removal rate and capacity after extended storage (>60 days) at 160ºF in air.

4.2.5.1   Capacity

Capacity measurements were performed on aged samples of uncoated DEB (lots x170 and x245) and polystyrene-coated DEB in an atmosphere of 5% H_2 in N_2 at a temperature of 77ºF (25ºC). The aged samples did not exhibit reduced capacity.

4.2.5.2   Rate

Rate measurements were performed on aged samples in an atmosphere of 5% H_2 in N_2 at a temperature of 77ºF (25ºC) (Figure 26). The aging process imparts an insignificant decrease on removal rate for uncoated DEB (lots x170 and x245) and polystyrene-coated DEB. Aged polybenzylmethacrylate-coated DEB exhibits a 50% decrease in removal rate. Hydrogen removal rates for all three aged materials exceed the programmatic minimum by at least 2 orders of magnitude.
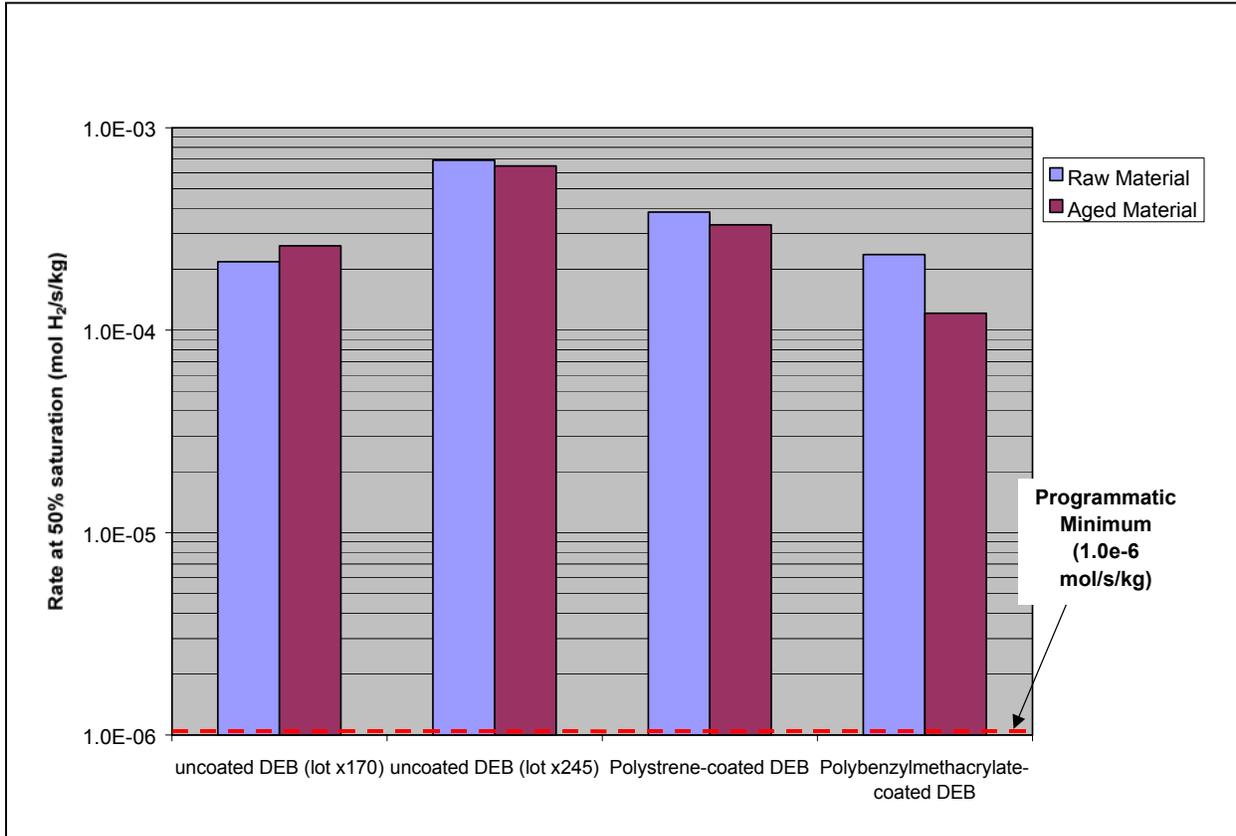
Figure 26. Effect of aging on hydrogen getter rates of uncoated DEB (lots x170 and x245), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 5% H_2 in nitrogen at a temperature of 77ºF (25ºC). Samples were aged for 60 days at 160°F in air.

4.2.6   Effect of Pressure

Tests to evaluate impact of pressure on getter performance were performed by Savannah River Technology Center (SRTC) in a static system (no flowing gas). The rates of hydrogen removal by uncoated DEB (lot x245) and polystyrene-coated DEB were measured at total pressures of 0 psig and 50 psig in atmospheres of 5.0% H_2 in nitrogen and 4.8% H_2 in air. Test results are summarized in Table 18. Pressure had no measurable effect on the hydrogen removal rate of uncoated DEB in nitrogen or air. Pressure reduced the hydrogen removal rate of polystyrene-coated DEB by approximately 65% (nitrogen atmosphere) to 70% (in air). The impacts of pressure are negligible as both materials exhibit removal rates that exceed the programmatic minimum by at least 2½ orders-of-magnitude.

36

Table 18. Effect of pressure on hydrogen removal rate (mole H_2 s-1 kg-1 at 50% capacity) for uncoated DEB (lot x245) and polystyrene-coated DEB. Temperature is 77ºF (25ºC) and the atmosphere is 5% hydrogen in nitrogen and hydrogen in air. Tests performed by SRTC, uncertainty is 50%. Minimum programmatic criteria is 1.0 x 10-6 mol H_2 s-1 kg-1.

Material	Pressure	H_2 in Air	H_2 in Nitrogen
Uncoated DEB (x245)	0 psig	5.44E-03	3.18E-03
	50 psig	4.94E-03	1.55E-03
Polystrene-coated DEB	0 psig	3.23E-03	8.60E-04
	50 psig	9.02E-04	2.99E-04

4.2.7   Reversibility

The potential of hydrogen absorbers to release hydrogen at elevated temperature is known as reversibility. DEB is not subject to reversible release of hydrogen because the hydrogen is chemically reacted to form stable covalent bonds. A test of reversibility was conducted as required by the consolidated test plan to verify this statement. In this test, a sample of uncoated DEB getter was loaded with hydrogen to full capacity, flushed with nitrogen at room temperature, then heated with continued nitrogen flushing to determine if hydrogen releases. In detail, a 0.50 g sample of uncoated DEB was sealed in the test column and flushed with nitrogen for approximately 120 minutes. Then the sample was heated to 70°C for approximately 120 minutes. In both portions of the test, effluent was monitored for hydrogen concentration. No hydrogen was detected in effluent gas at any portion of the test, indicating no release of hydrogen at room temperature or at 70°C.

4.2.8   Effect of Radiation - SRTC

Tests to evaluate impact of pressure on getter performance were also performed by SRTC in a static system. Uncoated DEB (lot x245) and polystyrene-coated DEB were exposed to a radiation dose of 2.5×10^{4} R in a cobalt-60 gamma source. The hydrogen absorption rate and capacity of the sample were then measured in atmospheres of 5.0% H_2 in nitrogen and 4.8% H_2 in air in the standard manner employed by SRTC. Test results are summarized in Table 19. Radiation had no measurable effect on the hydrogen removal rate of either material.

Table 19. Effect of radiation on hydrogen removal rate (mole H_2 s-1 kg-1 at 50% capacity) for uncoated DEB (lot x245) and polystyrene-coated DEB. Temperature is 77ºF (25ºC) and the atmosphere is 5% hydrogen in nitrogen and hydrogen in air. Tests performed by SRTC, uncertainty is 50%. Minimum programmatic criteria is 1.0 x 10-6 mol H_2 s-1 kg-1.

Material		H_2 in Air	H_2 in Nitrogen
Uncoated DEB (x245)	unirradiated	5.44E-03	3.18E-03
	irradiated	4.87E-03	3.48E-03
Polystrene-coated DEB	unirradiated	3.23E-03	8.60E-04
	irradiated	2.19E-03	1.22E-03

4.2.9   Temperature Effect Calculation

The hydrogenation reaction of DEB getter and the recombination reaction to form water are exothermic and will provide thermal output. The heat generated by these reactions, and the potential impact on the TRUPACT-II payload, are calculated and discussed below.

The hydrogenation reaction generates approximately 125 kJ mol^{-1} and the recombination reaction generates 286 kJ mol^{-1} (liquid water). Heat generation for 60 days at maximum hydrogen production (1.2 x 10^{-5} mol H$_2$ s^{-1}) for each of these reactions is: 1) recombination = 3.4 watts, and 2) hydrogenation of DEB = 1.5 watts.

The thermal output for the recombination reaction is greater than that of the hydrogenation reaction. In a worse case scenario, with all of the produced hydrogen taking part in the recombination reaction, the 3.4 W of heat generated is significantly below the 40 W maximum authorized for the TRUPACT-II payload. In a situation with some amount of the produced hydrogen taking part in each of the reactions, the heat generation will be even less than 3.4 W.

4.2.10   Evaluation of SRTC samples

Los Alamos National Laboratory (LANL) performed dynamic tests on the polymer getter and Savannah River Technology Center (SRTC) performed static tests on the DEB getter (uncoated and coated with polystyrene). Test parameters for measuring hydrogen removal rate included atmosphere (5% H$_2$ in nitrogen and 3% H$_2$ in air), temperature (160, 77, and -20°F), and presence of poison (1000 ppm carbon tetrachloride). Test results for polymer and DEB getters are presented in Tables 20 and 21, respectively. Dynamic testing (Table 20) verifies that polymer getter exceeds the programmatic minimum at the specified conditions.

Table 20. Hydrogen removal rate (mole H$_2$ s-1 kg-1 at 50% capacity) for polymer-zeolite getter in an atmosphere of 5% H$_2$ in nitrogen and 3% H$_2$ in air at temperatures of 160 to -20ºF (71.1 to –28.9ºC). Minimum programmatic criteria is 1.0 x 10-6 mol H$_2$ s-1 kg-1.

Atmosphere	Temperature		Rate	
	(ºF)	(ºC)	No Poison	Carbon Tetrachloride
5% H$_2$/Nitrogen	160	71	6.81E-04	6.55E-04
	77	25	5.93E-04	6.11E-04
	23	-29	1.83E-04	8.16E-05
3% H$_2$/Air	160	71	1.44E-03	1.38E-03
	77	25	1.28E-03	1.28E-03
	23	-29	9.10E-04	1.23E-03

Table 21. Comparison of hydrogen removal rate (mole H_2 s^{-1} kg^{-1} at 50% capacity) determined for uncoated DEB (lot x245) and polystyrene-coated DEB by dynamic and static test methods. Tests variables include atmosphere (5% H_2 in nitrogen and 3% H_2 in air), temperature (160, 77, and -20°F), and presence of poison (1000 ppm carbon tetrachloride). Minimum programmatic criteria is 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}. Significance of highlighted values are is discussed in the text.

Atmosphere	Temperature ^{o}F	^{o}C	Uncoated DEB, no poison			Uncoated DEB plus CCl4		
			dynamic testing	static testing	ratio static/dynamic	dynamic testing	static testing	ratio static/dynamic
Vacuum	160	71		4.07E-02			1.28E-02	
	77	[a]23		1.62E-03			7.43E-04	
	23	-29		1.29E-05			5.71E-06	
Nitrogen	160	71	[b]6.06E-04	1.75E-02	28.9	[b]4.42E-04	1.53E-02	34.6
	77	[a]23	6.91E-04	3.18E-03	4.6	1.89E-04	3.50E-03	18.5
	23	-29	[b]1.25E-04	6.68E-06	0.1		1.72E-06	
Air	160	71	7.34E-04	7.83E-03	10.7	6.85E-04	6.28E-03	9.2
	77	[a]23	6.53E-04	5.44E-03	8.3	6.53E-04	4.49E-03	6.9
	23	-29	5.17E-04	5.38E-05	0.1		8.19E-06	

Atmosphere	Temperature ^{o}F	^{o}C	Polystyrene-coated DEB, no poison			Polystyrene-coated DEB plus CCl4		
			dynamic testing	static testing	ratio static/dynamic	dynamic testing	static testing	ratio static/dynamic
Vacuum	160	71		3.14E-02			7.56E-03	
	77	[a]23		4.80E-04			1.56E-04	
	23	-29		2.33E-06			3.85E-07	
Nitrogen	160	71	2.81E-04	4.75E-03	16.9	4.28E-04	6.15E-03	14.3
	77	[a]23	5.22E-04	8.60E-04	1.6	1.37E-04	2.02E-04	1.5
	23	-29	1.75E-05	2.35E-06	0.1		1.63E-06	
Air	160	71	4.62E-04	2.65E-03	5.7	4.76E-04	4.09E-03	8.6
	77	[a]23	3.81E-04	3.23E-03	8.5	2.61E-04	1.53E-03	5.9
	23	-29	2.49E-04	2.63E-04	1.1		2.09E-05	

[a]Static tests were performed at 23°C and dynamic tests were performed at 25°C.

[b]Uncoated DEB lot x170 used in this test.

Test results comparing DEB getter performance as determined by dynamic and static test methods are presented in Figures 27 and 28. In an atmosphere of nitrogen (±carbon tetrachloride) and at a temperature of 160°F (71°C), hydrogen removal rates are approximately 15x (polystyrene-coated DEB) to 30x (uncoated DEB) faster as determined by the static method compared to the dynamic testing method.
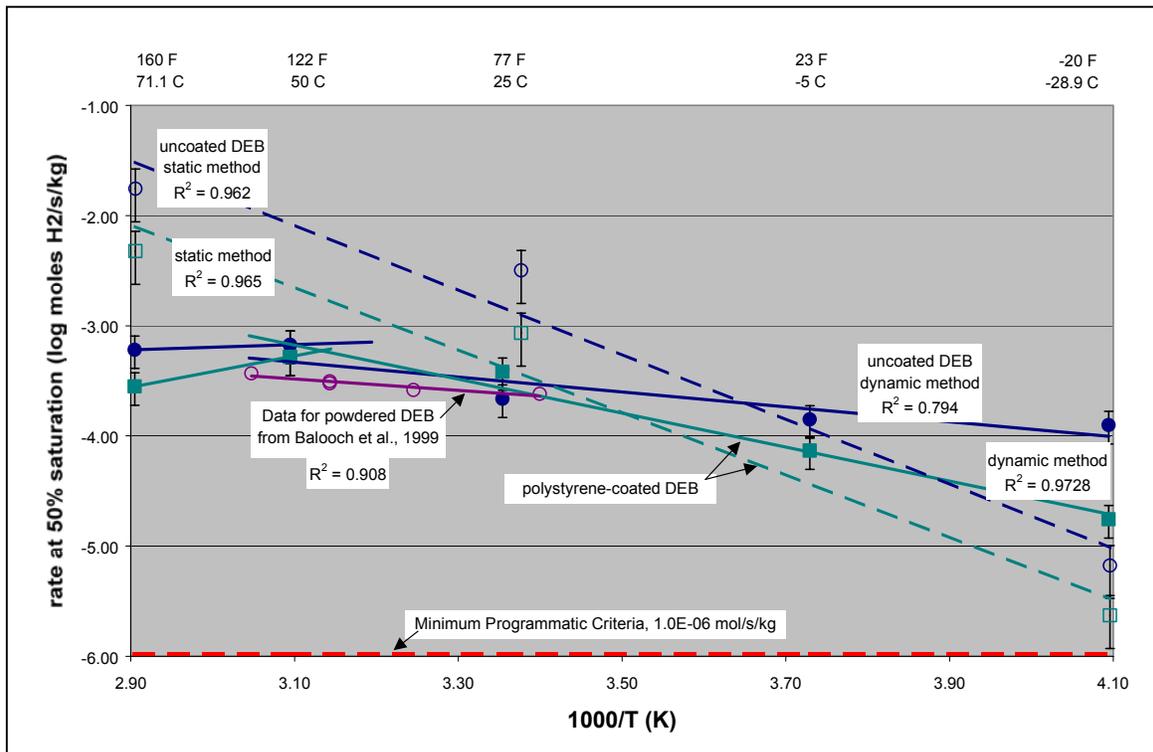
Figure 27. Arrhenius plot (hydrogen removal rate vs. temperature) determined for uncoated DEB and polystyrene-coated DEB by dynamic (solid lines and filled symbols) and static (dashed lines and open symbols) test methods. Tests were performed in an atmosphere of 5% H_2 in nitrogen at temperatures of 160 to -20°F (71.1 to –28.9°C). The hydrogen removal rate is plotted as log mole H_2 s^{-1} kg^{-1} at 50% capacity and the temperature is plotted as reciprocal Kelvin multiplied by 1000. Error bars represent maximum uncertainty. Plotted for comparison are data for powdered DEB reported by Balooch *et al*., 1999 for the temperature range of 21 to 55°C. Also plotted for comparison is the minimum programmatic criteria of 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}.

In air (±carbon tetrachloride) and at a temperature of 160°F (71°C), the rates are approximately 5x (polystyrene-coated DEB) to 10x (uncoated DEB) faster as determined by the static method compared to the dynamic testing method. At 77°F (25°C), the rates determined by the static method range from 0.5 to 20x faster compared to the dynamic method. At 23°F (-29°C), rates determined by the static method are approximately 10% as fast as rates determined in the dynamic method for uncoated DEB (air and nitrogen atmospheres) and polystyrene (nitrogen atmosphere). At this temperature, the rates determined for polystyrene-coated DEB in air are approximately equal in both methods.

In dynamic testing, uncoated DEB and polystyrene-coated DEB exhibit removal rates that exceed the programmatic minimum by at least one order-of-magnitude. The same conclusion may be drawn from results derived with static testing with the following exceptions (highlighted values in Table 21). The programmatic minimum is exceeded by approximately one-half order of magnitude at 23°F (-29°C) for uncoated DEB in a vacuum (with carbon tetrachloride) and in an atmosphere of nitrogen (without carbon tetrachloride). The programmatic minimum is exceeded by approximately 2x for:
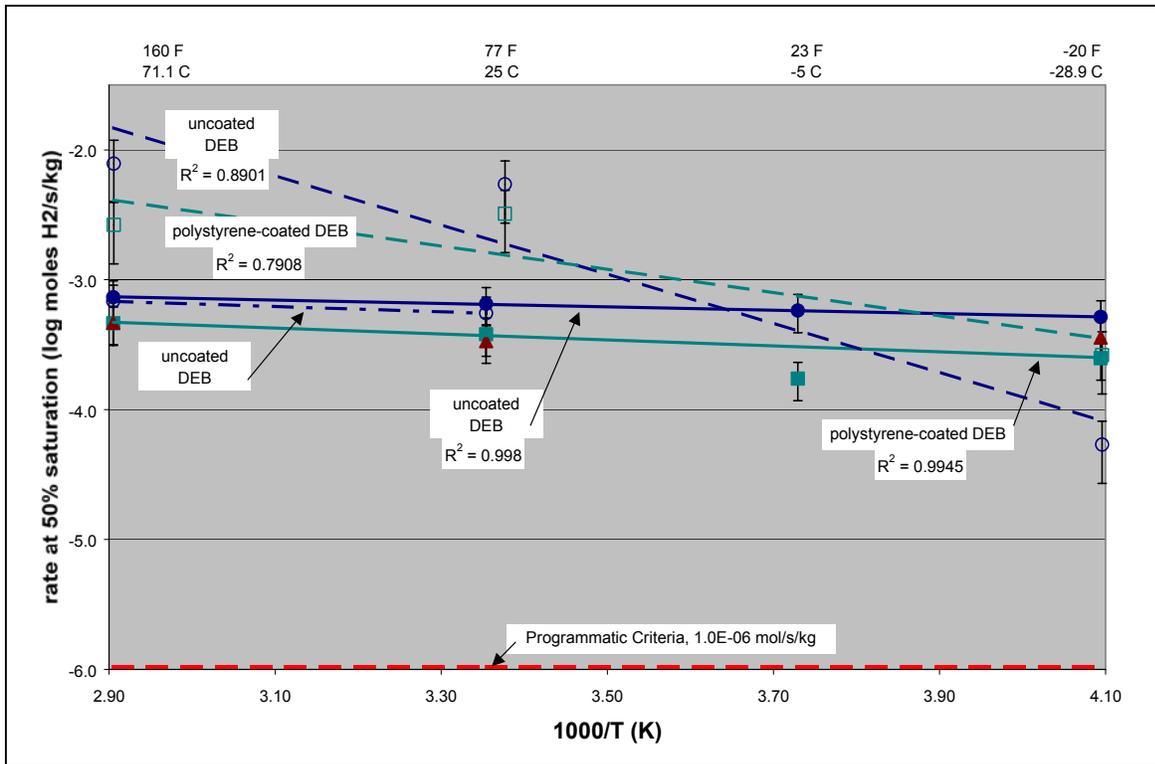
Figure 28. Arrhenius plot (hydrogen removal rate vs. temperature) determined for uncoated DEB and polystyrene-coated DEB by dynamic (solid lines and filled symbols) and static (dashed lines and open symbols) test methods. Tests were performed in an atmosphere of hydrogen in air at temperatures of 160 to -20ºF (71.1 to –28.9ºC). The hydrogen removal rate is plotted as log mole H_2 s^{-1} kg^{-1} at 50% capacity and the temperature is plotted as reciprocal Kelvin multiplied by 1000. Error bars represent maximum uncertainty. Plotted for comparison is the minimum programmatic criteria of 1.0×10^{-6} mol H_2 s^{-1} kg^{-1}.

- uncoated DEB in an atmosphere of nitrogen (with carbon tetrachloride),

- polystyrene-coated DEB in a vacuum (without carbon tetrachloride), and

- polystyrene-coated DEB in nitrogen (with and without carbon tetrachloride).

In addition, static testing suggests that polystyrene-coated DEB fails to meet the programmatic minimum at 23ºF (-29ºC) in a vacuum with carbon tetrachloride. The reason for the differences between static and dynamic testing in these instances is not currently known. It is also not known why dynamic testing yields overall results that differ in detail from the static results reported herein but are consistent with the published values of Balooch et al. (1999). The data of Balooch et al. (1999) were also determined in a static test method. It is important to note, however, that the performance of DEB getter in air exceeds the programmatic minimum by approximately two orders-of-magnitude.

SRTC also performed capacity measurements on the DEB getter (uncoated and coated with polystyrene) using static test methods. Test results are presented in Table 22. Static capacity measurements of uncoated DEB are within 90-95% of the theoretical stoichiometric capacity of DEB

(10.86 mol kg^{-1}). Capacity measurement of polystyrene-coated DEB are within 72-82% of the stoichiometric capacity. Capacity measurements on irradiated samples of both getter materials provide similar results. The polystyrene coating is a very small fraction of the total mass of getter material, much less than 1% (by weight). Therefore, it is not known why polystyrene-coated DEB yields a smaller capacity compared to uncoated DEB and to the stoichiometric capacity. It is also currently not known why static measurements provide different capacity results compared to dynamic measurement.

Table 22. Capacity data (mol kg^{-1}) for DEB samples as determined by SRTC in the static test method. The theoretical stoichiometric capacity of DEB is 10.86 mol kg^{-1}. Uncertainty in static test method is $\pm$ 5%.

	Unirradiated	Method of H_2 Addition	Irradiated	Method of H_2 Addition
Uncoated DEB	10.34	expand rapidly and heat	10.28	leak slowly and heat
	9.67	leak slowly		
Polystyrene-coated DEB	8.88	expand rapidly and heat	---	---
	7.86	expand rapidly*	8.27	expand rapidly*
	7.82	leak slowly	---	---

* There was essentially no difference in the absorption curves for these two samples, but the irradiated sample test ran almost 3 times longer.

5.   CONCLUSIONS

The goal of this program was to investigate the potential for using coated hydrogen getter materials in TRUPACT containers to prevent the build up of hydrogen to a dangerous level. The hydrogen getter investigated by the INEEL/LANL team was a precious metal catalyzed hydrogenation system. It is a combination of palladium dispersed on carbon and a chemical named 1,4-bis(phenylethynyl)benzene (DEB). The material is delivered as irregular shaped small particles approximately 1-2 mm in diameter. The triply-bonded carbon atoms in the DEB, in the presence of the palladium, irreversibly react with the hydrogen to form the corresponding saturated alkane compounds.

It is known that many catalyst systems can be negatively affected by exposure to certain chemical poisons. Since a number of potential catalyst poisons are present in the drums that also are producing the hydrogen, studies into the impact of the poisons on this specific getter and means for protecting the getter prompted this project. The INEEL/LANL team chose to encapsulate the getter particles with a semipermeable polymeric coating that would allow the hydrogen to enter and be retained. At the same time the polymeric coating inhibits, or at least reduces to an acceptable level, the entry of the poisons into the getter particles.

A Consolidated Testing Plan for the Phase 2 was developed and followed. The proposed getter formulations (coated and uncoated) were subjected to tests that determined the performance of the getters with regards to capacity, operating temperature range (with hydrogen in nitrogen and in air), hydrogen concentration, poisons, aging, pressure, reversibility, and radiation effects. The conclusions that can be made up to this point are: *1) All of the polymer coated materials performed well above the figure of merit, and 2) Even the uncoated getter performed above the figure of merit.*

The conclusions that can be stated about the getter performance relative to the programmatically specified parameters include:

- Over the complete temperature range and maximum poison concentration 5.7 kg of getter provided the required capacity and rate,
- In the temperature range of 160°F to 77°F the getter rates exceed the minimun programmatic requirement by at least 100X,
- In the temperature range of 23°F to –20°F the getter rates exceed the minimum programmatic requirements by at least 10X,
- Reducing the hydrogen concentrations from 5% to 1% in nitrogen had no significant effect on the rate,
- Reaction rates are higher in air than in nitrogen due to recombination plus gettering reactions,
- The gettering reaction was not found to be sensitive to pressure, radiation, and was shown not to be reversible, and
- Under the worst case conditions (low temperature, air, and in the presence of CCl_4), the observed rate was greater than 8X the minimum programmatic requirement.

6. REFERENCES

Balooch, M., Wang, W.-E., and Kirkpatrick, J. R. (2001) Hydrogen uptake mechanism of a silicone-rubber DEB getter mixture, *Journal of Polymer Science: Part B: Polymer Physics* **39**, 425-431.

Balooch, M., Wang, W.-E., and Lemay, J. D. (1999) Thermochemical properties of the hydrogen getter DEB, *Journal of Nuclear Materials* **270**, 248-252.

NRC, 1996, *Safety Analysis Report for the TRUPACT-II Shipping Package,* Revision 16, NRC Docket No. 9218, Washington, D.C., U.S. Nuclear Regulatory Commission.

Sheppod *et al.* (T. J. Sheppod, L. R. Gillion, and H. M. Smith), 1989, "Organic Getter Materials for the Removal of Hydrogen and its Isotopes," Presented at the Fourth International Conference on the Effects of Hydrogen on the Behavior of Materials, Moran, Wyoming, September 12–15, **1989**.

Smith, H.M., and T.J. Sheppod, 1990, "Hydrogen-Tritium Getters and Their Applications," Presented at the Radioluminescent Lighting Technology Transfer Conference, Annapolis, Maryland, September 25–26, 1990.

Uludag-Demirer, S. and A. R. Bowers, Adsorption/Reduction Reactions of Trichloroethylene by Elemental Iron in the Gas Phase: The Role of Water, Environ. Sci. Technol., **34**, 4407-4412, 2000.