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DEVELOPMENT OF HYDROGEN GAS GETTERS FOR TRU WASTE

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ABSTRACT

Alpha radiolysis of hydrogenous waste and packaging materials generates hydrogen gas in radioactive storage containers. For this reason, the flammable gas (hydrogen) concentration in waste shipment containers (Transuranic Package Transporter-II or TP-II containers) is limited to the lower explosion limit of hydrogen in air (5 vol%). The use of hydrogen getters is being investigated to prevent the build up of hydrogen during storage and transport of the TP-II containers (up to 60 days). Preferred hydrogen getters are solid materials that scavenge hydrogen from the gas phase and chemically and irreversibly bind it in the solid state. One proven getter, 1,4-bis (phenylethynyl)benzene or DEB, belongs to a class of compounds called alkynes, which are characterized by the presence of carbon-carbon triple bonds. These carbon atoms will, in the presence of suitable catalysts such as palladium, irreversibly react with hydrogen to form the corresponding saturated alkane compounds. Because DEB contains two triple bonds, one mole of DEB reacts with 4 moles of hydrogen. The standard formulation for the "DEB getter" is a mixture of 75% DEB and 25% carbon catalyst (5% palladium on carbon).

Certain chemicals such as volatile organic compounds (VOCs) are known to "poison" and reduce the activity of the catalyst. Therefore, in addition to the standard formulation, a semi-permeable barrier that encapsulates and protects the getter and its catalyst from poisons was also developed. The uncoated and polymer coated getter formulations were subjected to tests that determined the performance of the getters with regard to capacity, operating temperature range (with hydrogen in nitrogen and in air), hydrogen concentration, poisons, aging, pressure, reversibility, and radiation effects. This testing program was designed to address the following performance requirements: 1) Minimum rate for hydrogen removal of 1.2E-5 moles hydrogen per second for 60 days; 2) Sufficient getter material within the TP-II to ensure that no more than 50% of getter material is consumed during the 60 days; and 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.

All of the coated getters as well as the uncoated DEB performed well above the performance requirements. Coating the DEB with polymers did not significantly enhance getter performance in the presence of poisons relative to uncoated DEB. The next phase of the project is to evaluate a scaled-up getter package for performance under waste shipping conditions anticipated in the TP-II.

INTRODUCTION

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 [1].

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 Los Alamos National Laboratory (LANL) and Savannah River Site, and americium-contaminated wastes at Hanford, Idaho National Engineering and Environmental Laboratory (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 hydrogen getter allows for up to 5 grams of heat source plutonium in the drum. This scenario minimizes volume expansion for these waste streams.

The purpose of this joint LANL/INEEL project is to determine the efficacy of DEB in supporting shipment of wastes do not meet transportation requirements for hydrogen gas concentration. Both uncoated DEB and microencapsulated DEB (hydrogen-permeable polymer coatings) are evaluated. More detailed results are presented in a joint LANL/INEEL report [2].

TECHNOLOGY CONCEPT AND FUNCTION

All of the getters investigated by all parties in the 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 provides a semipermeable barrier that allows the hydrogen through to the getter and prevents the permeation of the poison. The results for the coated and uncoated getter systems are reported in this document. If a suitable encapsulant can be found, the proposed approach has the advantage of working regardless of the amount of poison present.

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) belongs to a class of compounds called alkynes, which are characterized by the presence of carbon-carbon triple bonds (Figure 1). 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 [3, 4]. 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.

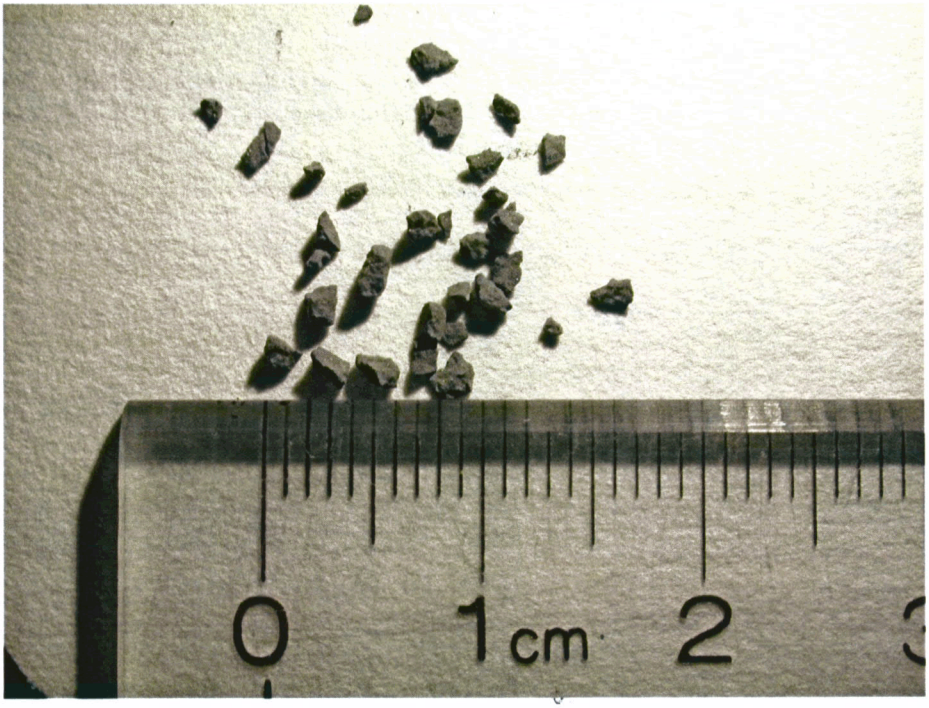

Figure 2. Photograph of the uncoated DEB getter (X20).

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.

GETTER COATING

Initial tests were performed 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, 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.

A subsequent feasibility study consisting of two prime components was performed: 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? 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.

Polymer Permeability

The first task 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. 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, ~5 $x10^{-10}$ 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. 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. Some of the later polymers were tested against a reduced set of gases. Several polymers met the requirements.

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 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.

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.

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.

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). 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 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 scanning electron microscopy (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 um (particle volume = 180,000,000 um^3). The average particle size was determined with a sonic sifter, using 8 sieves between 300 and 1180 um. The calculations assume spherical particles.

Initial Performance

Dynamic testing of performance is performed by flowing a gas mixture (typically 5 % hydrogen in nitrogen) over a sample of the getter material at a constant temperature. The thinnest coating of PVC was sufficient to prevent any permeation of hydrogen through to the active getter material. Experiments conducted at both 20 and 40 °C obtained the same result. All of the tests 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. Tests showed that both the gettering reaction and the recombination reaction are rapidly poisoned by CCl_4.

ADVANCED TESTING

The samples considered to have the best properties (permeability to H_2 relative to poisons) were tested for H_2 getter property testing, as listed in Table 1.

Table 1. A listing of the getter samples tested for H_2 getter properties.

	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

Additional dynamic testing was performed in the same manner as initial performance testing. An automated data acquisition system was used. Influent and effluent hydrogen concentrations were measured, and getter performance was benchmarked at a hydrogen removal rate at 50% DEB 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}). 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 1). 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.

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 2). 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 2. 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 77°F (25°C). 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

Capacity of Getter Materials

Capacity measurements were performed on uncoated DEB lot x170 and lot x245. 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.

Empirically 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 is smaller than the variation in hydrogen removal rate (at 50% saturation) measured for these lots. This difference is due to the method of calculating rate based on theoretical capacity. Rates that are calculated from empirically measured capacities produce results that are consistent with the empirically measured variation in hydrogen capacity (Table 3). 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 3. 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%

Operating Temperature Range

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

Rate measurements were performed on all materials (Table 1) in an atmosphere of 5% H_2 in N_2 over the temperature range of 160 to 77°F (71.1 to 25°C). Test results are summarized in Table 4. In general, uncoated DEB exhibits the largest rate of hydrogen removal relative to the coated DEB materials. However, all materials exhibit 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.

Table 4. 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 23°F (71.1 to -5°C). Removal rates are also reported for uncoated DEB (lot x170), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB at a temperature of -20°F (–28.9°C). Minimum programmatic criteria is 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}.

T (C)	T (K)	1000/T (K)	Uncoated DEB (lot x170)	Polystrene	Polystyrene-co-methylmethacrylate	Polyiospropylmethacrylate	Polybenzylmethacrylate	Kynar (PVDF)	CMS-3
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
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
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
-5	268	3.73	1.41E-04	7.36E-05	1.84E-04		6.21E-05	1.63E-04	1.28E-04
-28.9	244	4.09	1.25E-04	1.75E-05			1.24E-05		

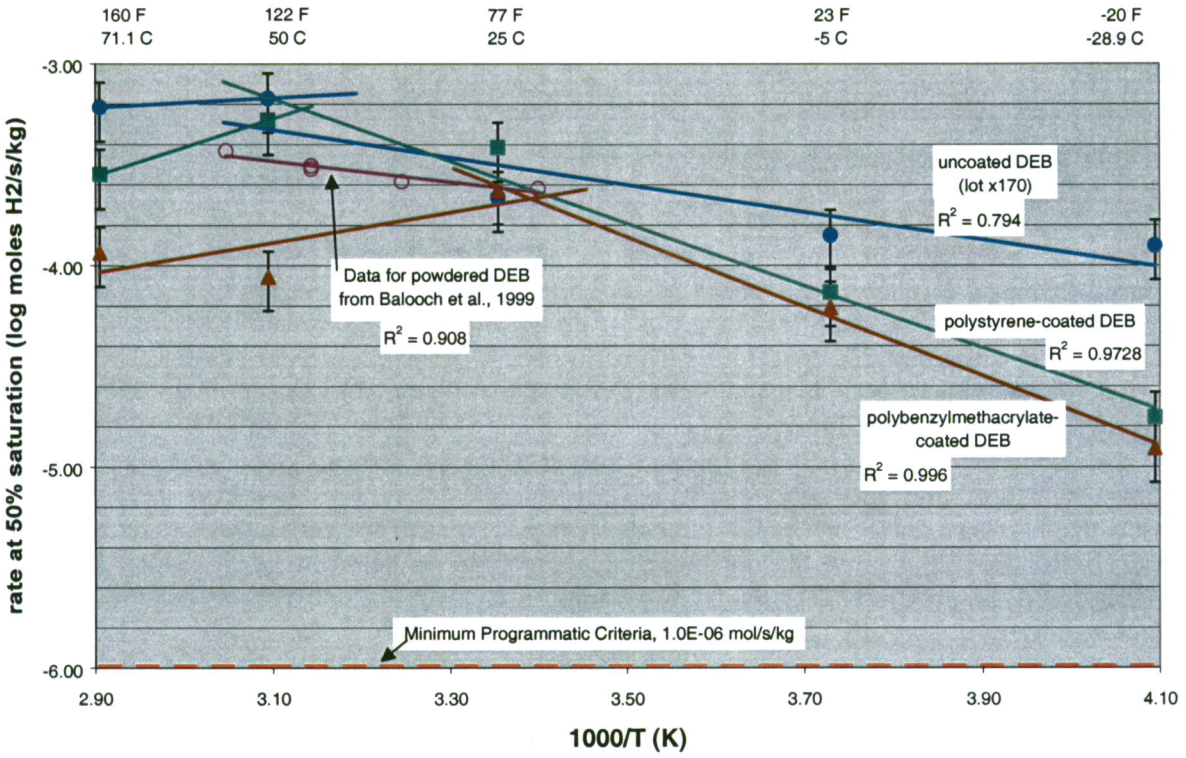

Figure 3. Arrhenius plot (hydrogen removal rate vs. temperature) for uncoated DEB (lot x170), polystyrene-coated DEB, and polybenzylmethacrylate-coated DEB in an atmosphere of 5% H_2 in nitrogen at temperatures of 160 to -20°F (71.1 to –28.9°C). The hydrogen removal rate is plotted as log mole H_2 s^{-1} 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 [5] for the temperature range of 21 to 55°C.

Results from tests performed in nitrogen for the limited temperature range (160 to 23°F, 71.1 to -5°C) 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 -20°F (-28.9°C). Test results for these three materials are summarized in Table 4 and presented as Arrhenius plots (Figure 3) for the full temperature interval (160 to -20°F, 71.1 to –28.9°C). All three materials exhibit hydrogen removal rates that exceed the programmatic minimum for this temperature range. At -20°F (-28.9°C), 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 -20°F (50 to –28.9°C). Arrhenius behavior is exhibited by polybenzylmethacrylate-coated DEB over a narrower temperature interval of 77 to -20°F (25 to –28.9°C). A slope change of the Arrhenius plots occurs at temperatures greater than 122°F (50°C) for uncoated DEB and polystyrene-coated DEB and at a temperature greater than 77°F (25°C) 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 160°F (71.1°C) exhibited physical changes, including adhesion of individual grains as sticky masses

and plugs. Similar changes were observed in 122°F (50°C) tests with uncoated DEB and polystyrene-coated DEB. Polybenzylmethacrylate-coated DEB did not exhibit these changes in tests performed below 160°F (71.1°C). 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.

Little has been published on the kinetics of DEB hydrogenation. Balooch *et al.* [5] 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 3 and agrees reasonably well with the kinetic data determined in this study for uncoated DEB. Balooch *et al.* [6] 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.* [6] 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. 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 -20°F (71.1 to –28.9°C). Test results for these three materials are summarized in Table 5. All three materials exceed the programmatic minimum by approximately 2 to 2.5 orders of magnitude for this temperature range.

Table 5. 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 -20°F (71.1 to –28.9°C). Minimum programmatic criteria is 1.0 x 10^{-6} mol H_2 s^{-1} kg^{-1}.

T (C)	T (K)	1000/T (K)	Uncoated DEB (lot x170)	Uncoated DEB (lot x245)	Polystrene	Polybenzylmethacrylate
71.1	344	2.90	6.82E-04	7.34E-04	4.62E-04	4.68E-04
25	298	3.35	5.51E-04	6.53E-04	3.81E-04	3.37E-04
-5	268	3.73		5.79E-04	1.73E-04	1.39E-04
-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 23°F (-5°C). The cause of this anomaly is uncertain, but it may be the result of proximity to the freezing point of water.

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.

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 77°F (25°C). 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.

Poison Effects

The compounds selected for screening as potential poisons are listed in Table 6. 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 6. 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

Rate measurements were performed on all materials (Table 1) in an atmosphere of 5% H_2 in N_2 at a temperature of 77°F (25°C) in the presence of the poisons listed in Table 6. The effect of poisons on hydrogen removal rate at 77°F (25°C) is summarized in Table 7. Poisons impact the hydrogen removal rate of all of the materials at 77°F (25°C). However, all materials exhibit removal rates that exceed the programmatic minimum by at least 1 order of magnitude.

At 77°F (25°C), toluene actually enhances hydrogen removal rates for all materials that were tested (Table 7). 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 1) in an atmosphere of 5% H_2 in N_2 at a temperature of 160°F (71.1°C) in the presence of carbon tetrachloride. The effect of carbon tetrachloride at 160°F (71.1°C) is summarized in Table 8. 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 160°F (71.1°C), all materials exhibit removal rates that exceed the programmatic minimum in the presence of carbon tetrachloride by at least 1 order of magnitude.

Table 7. Effect of poisons on hydrogen removal rates (mole H_2 s-1 kg-1) of DEB and coated DEB at 77°F (25°C) 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	

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 are consistent with the permeability data measured for polymer coatings. The data 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.

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 77°F (25°C) in the presence of the organic poisons listed in Table 6. 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 77°F (25°C), all three materials exhibit removal rates that exceed the programmatic minimum by approximately 2 orders of magnitude.

Table 8. Effect of carbon tetrachloride on hydrogen removal rates (mole H_2 s-1 kg-1) of DEB and coated DEB at 160°F (71.1°C) 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

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 160°F (71.1°C) in the presence of carbon tetrachloride. Carbon tetrachloride does not exhibit a measurable effect on removal rates for hydrogen in air at 160°F (71.1°C).

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 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.

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 limit 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 77°F (25°C) 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. 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.

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 160°F in air.

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 77°F (25°C). The aged samples did not exhibit reduced capacity.

Rate measurements were performed on aged samples in an atmosphere of 5% H_2 in N_2 at a temperature of 77°F (25°C). 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.

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. 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.

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.

Effect of Radiation

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 x 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. Radiation had no measurable effect on the hydrogen removal rate of either material.

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. 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 H2 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.

Inter-Laboratory Comparisons

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). Dynamic testing verifies that polymer getter exceeds the programmatic minimum at the specified conditions.

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.

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. 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 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 23°F (-29°C) 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.* [5]. The data of Balooch *et al.* [5] 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. 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.

CONCLUSION

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.

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 stated about the getter performance include:

1) Over the complete temperature range (160 to –20 F) and maximum poison concentration (1000 parts per million carbon tetrachloride), 5.7 kg of DEB provided the required capacity and rate;
2) In the temperature range of 160 to 77 F, getter rates exceed the specified minimum hydrogen removal rate by at least 100x;
3) In the temperature range of 23 to –20 F, the getter rates exceed the minimum hydrogen removal rate by at least 10x;
4) Reducing the hydrogen concentrations from 5% to 1% in nitrogen had no significant effect on the gettering rate;
5) Reaction rates are higher in air than in nitrogen due to recombination plus gettering reactions;

6) The gettering reaction was not found to be sensitive to pressure or radiation, and was shown to be irreversible; and
7) Under the worst-case conditions (low temperature, air, and in the presence of carbon tetrachloride), the observed rate was greater than 8x the minimum performance requirement.

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