

Scaled Testing of Hydrogen Gas Getters for Transuranic Waste

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ABSTRACT

Alpha radiolysis of hydrogenous waste and packaging materials generates hydrogen gas in radioactive storage and shipment containers. Hydrogen forms a flammable mixture with air over a wide range of concentrations (5% to 75%), and very low energy is needed to ignite hydrogen-air mixtures. For these reasons, the concentration of hydrogen in waste shipment containers (Transuranic Package Transporter-II or TRUPACT-II containers) needs to remain below the lower explosion limit of hydrogen in air (5 vol%). Accident scenarios and the resulting safety analysis require that this limit not be exceeded.

The use of "hydrogen getters" is being investigated as a way to prevent the build up of hydrogen in TRUPACT-II containers. Preferred getters are solid materials that scavenge hydrogen from the gas phase and chemically and irreversibly bind it into the solid state. In this study, two getter systems are evaluated: a) 1,4-bis (phenylethynyl)benzene or DEB, characterized by the presence of carbon-carbon triple bonds; and b) a proprietary polymer hydrogen getter, VEI or TruGetter, characterized by carbon-carbon double bonds. Carbon in both getter types may, in the presence of suitable precious metal catalysts such as palladium, irreversibly react with and bind hydrogen. With oxygen present, the precious metal may also eliminate hydrogen by catalyzing the formation of water. This reaction is called catalytic recombination.

DEB and VEI performed satisfactorily in lab scale tests using small test volumes (ml-scale), high hydrogen generation rates, and short time spans of hours to days. The purpose of this study is to evaluate whether DEB and VEI perform satisfactorily in actual drum-scale tests with realistic hydrogen generation rates and time frames. The two getter systems were evaluated in test vessels comprised of a Gas Generation Test Program-style belljar and a drum equipped with a composite drum filter. The vessels were scaled to replicate the ratio between void space in the inner containment vessel of a TRUPACT-II container and volume of a payload of seven 55-gallon drums. The tests were conducted in an atmosphere of air for 60 days at ambient temperature (15 to 27°C) and a scaled hydrogen generation rate of 2.60E-07 moles hydrogen per second (0.35 cc/min).

Hydrogen was successfully "gettered" by both systems. Hydrogen concentrations remained below 5 vol% (in air) for the duration of the tests. However, catalytic reaction of hydrogen with carbon triple or double bonds in the getter materials did not take place. Instead, catalytic recombination was the predominant

mechanism in both getters as evidenced by 1) consumption of oxygen in the belljars; 2) production of free water in the belljars; and 3) absence of chemical changes in both getters as shown by NMR spectra.

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 (WIPP). The Nuclear Regulatory Commission (NRC) has imposed a flammable gas concentration limit on CH-TRU waste transported in the TRUPACT-II to minimize the potential for containment loss due to fire or explosion. For hydrogen, this limit is set at the lower explosive limit of 5 vol% hydrogen in air. Accident scenarios and the resulting safety analysis, developed as part of the TRUPACT-II SARP, require that this limit not be exceeded.

Hydrogen gas generation and accumulation is the result of alpha radiolysis of hydrogenous waste and packaging materials. The combination of high activity wastes with multiple layers of packaging has produced quantities of wastes that do not meet transportation requirements for hydrogen gas concentration.

Los Alamos National Laboratory (LANL) and Idaho National Laboratory (INL) have been engaged in the DOE's multi-year "Improved Hydrogen Gas Getters for TRU Waste" program to evaluate materials that will prevent the build up of hydrogen during the storage and transport of TRUPACT-II containers.[1] The program focused on "hydrogen getters", materials that scavenge hydrogen from the gas phase and irreversibly bind it in the solid phase. Getters use a precious metal hydrogenation catalyst, such as palladium, to chemically react free molecular hydrogen with some type of unsaturated organic/polymeric material. In the initial stages of the project, hydrogen getters were evaluated at the laboratory scale using small test volumes (ml-scale), high hydrogen generation rates, and short time spans of hours to days.[1-4] Two getter systems were ultimately selected as suitable: a) 1,4-bis (phenylethynyl)benzene or DEB, characterized by the presence of carbon-carbon triple bonds; and b) a proprietary polymer hydrogen getter, VEI or TruGetter, characterized by carbon-carbon double bonds. Carbon in both getter types may irreversibly react with and bind hydrogen. In the presence of oxygen, the precious metal catalyst may also eliminate hydrogen by catalyzing the formation of water. This reaction is called catalytic recombination.

The purpose of this final phase of the project is to evaluate whether DEB and VEI perform as anticipated when deployed in the TRUPACT-II. To achieve this objective, getter assemblies were tested in drum-scale tests with realistic hydrogen generation rates and time frames (60 days). The tests were conducted at ambient temperature (15 to 27°C) in an atmosphere of air. Budget constraints precluded evaluation of two issues a) whether DEB and VEI perform at cold temperature (-29°C) in an atmosphere containing volatile organic constituents that compete with hydrogen; and b) whether DEB and VEI fuse at higher temperature (71°C), leading to adverse impact on getting rates.

Hydrogen Getter Concept and Function

DEB 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, 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 palladium 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.

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). The standard formulation for the “DEB getter” is a mixture of 75% DEB and 25% carbon catalyst (5% palladium on carbon). It has been shown to be stable in the absence of hydrogen for up to 18 months (at +70°C, under nitrogen). DEB reacts rapidly, exothermically (~30 Kcal/mole hydrogen), and irreversibly with hydrogen. It has a capacity of 240 to 330 cm³ 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 cm³/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.

VEI or TruGetter, a proprietary polymer hydrogen getter, is another other potential hydrogen getter being tested.[5, 6] Both DEB and VEI are based upon the catalytic reaction of hydrogen with carbon triple or double bonds, respectively. Both getters contain a palladium or platinum catalyst that may catalyze the recombination of hydrogen with oxygen to form water.

TEST METHODS

The two getters (DEB and VEI) were evaluated in scaled replicas of a TRUPACT-II containing a payload of seven 55-gallon drums. A replicate test was simultaneously conducted with DEB to take advantage of a third available test vessel. Hydrogen was introduced into the drum replicas at a known rate. The drums were equipped with a composite filter to permit diffusion of hydrogen out of the drum and into the headspace of the TRUPACT-II replica. Tests were conducted in an atmosphere of air for 63.9 days at ambient temperature (15 to 27°C). Both *in-situ* and discrete gas sampling was performed to monitor changes in hydrogen and oxygen concentrations during the course of the tests. Nuclear magnetic resonance spectroscopy was performed on the getters to determine the extent of hydrogenation that had occurred during testing.

Design and Measurements

Test design and implementation was based on results from laboratory testing performed in the initial stages of the project [1-4], recommendations from the American Society of Mechanical Engineers Peer Review Panel [7, 8], and discussions with WIPP operations personnel¹. Waste handling considerations require a deployment configuration with a getter superstructure of horizontally placed “cans” of approximately 4-inch diameter and 12-inch length, and 6-inch minimum axis separation, with vertical access for both 3 and 4 point Adjustable Center of Gravity Lift Fixture arms. The getter assemblies used in the tests were scaled to this configuration.

The tests used aspects of the Gas Generation Test Program (GGTP) of the LANL TRU Waste Characterization/Certification Project. Elements of the GGTP were used because GGTP technology was previously approved for use at WIPP and because this technology was successfully employed in the WIPP program. In the GGTP, hydrogen gas generation rates were determined for transuranic waste using gas generation test canisters (herein referred to as “belljars”). The belljar is a stainless canister that encapsulates a 55-gallon waste drum and accumulates the gases generated from the drum. In this manner, off-gases generated from the waste drum are measured and hydrogen generation rate of the drum calculated.

¹Hydrogen Gas Getters Evaluation Program Meeting, September 10-11, 2002, Carlsbad, New Mexico.

In each test, one belljar vessel and one drum were used as a scale replica of the TRUPACT-II containing a payload of seven 55-gallon drums. The free volume inside the belljar was scaled to the free volume within the inner containment vessel (ICV) of the TRUPACT-II. The void space in the ICV of a TRUPACT-II is 2.68 times greater than the volume of a payload of seven 55-gallon drums. A drum equipped with a composite drum filter (diffusivity of $1.16\text{E}-05$ mol/s/mf) was scaled to these dimensions in order to test the getter assembly under conditions that represent deployment. The resultant dimensions for the bell jar and drum are listed in Table I.

Table I. Design Specifications

Specifications for TRUPACT-II containing 7 drums
headspace (void space) in the ICV of TRUPACT-II = 3906 liters
volume of seven 55-gal drums = 1456 liters
ratio of headspace volume in ICV: volume of seven 55-gal drums = 2.68
Dimensions of GGTP-style belljar tests scaled to TRUPACT-II containing 7 drums
bell jar volume = 304 liters
drum volume = 82.6 liters
headspace volume of bell jar containing 1 drum = 221.4 liters
ratio of bell jar headspace volume: drum volume = 2.68
ratio of scaled drum to 55-gal drum = 0.40

The hydrogen generation rate is based on matrix-depleted G values in the TRUPACT-II SAR and a payload of seven drums, which results in the maximum hydrogen generation rate per drum and provides bounding test conditions. The target hydrogen generation rate, assuming 40 watts per TRUPACT-II and a hydrogen G-value of 1.09, is $4.54\text{E}-06$ moles per second or 23.54 moles in 60 days in a TRUPACT-II. Since the rate per drum is simply a function of the number of drums per TRUPACT-II, the hydrogen generation rate for each of seven drums in a TRUPACT-II shipment is $6.49\text{E}-07$ moles per second. Scaling this rate to GGTP-style tests with a drum of appropriate dimensions (Table I) yields a hydrogen generation rate of $2.60\text{E}-07$ moles per second per test drum ($1.56\text{E}-05$ mol/minute or 0.35 cc/min).

Industrial grade hydrogen (99.95% pure) was introduced into the drum for each test via an Omega flow meter adjusted to the proper rate. Continuous hydrogen measurements were made in each of the three drums with a Dual Loop Hydrogen Analyzer manufactured by Meggitt Safety Systems, Inc. Temperature was monitored inside each belljar, on the external surface of each belljar, and in test room using Omega type T thermocouples. Pressure was monitored inside each belljar and in the test room using Omega pressure transducers. A computer data logging system was employed to record ambient temperature, belljar temperatures, pressure inside the belljar, ambient pressure, flow rate of injected hydrogen, and concentration of hydrogen as continuously monitored by the Meggitt hydrogen sensors. The data logging system consisted of FieldPoint[®] data logging modules that collected data from the various sensors and transmitted these data via Ethernet to a central computer. The computer processed these data using LabView[®] software.

Samples of the belljar and drum headspace were periodically collected using sampling procedures described in Gas Test Canister Operations (TWCP-DTP-1.2-056). These samples were analyzed for

hydrogen and oxygen using gas chromatography as described in Gas Chromatography Determination of Hydrogen in Gas Generation Test Canisters (TWCP-DTP-1.2-057, R.3). Headspace samples were collected daily in the first week of each test, twice during the second week of each test, and weekly thereafter. Maximum uncertainties (1 standard deviation) determined for hydrogen and oxygen analyses are 3.4% and 1.8%, respectively. Several different standards were used during different phases of the tests, depending on the relative concentrations of hydrogen and oxygen present. The standards used and detailed information regarding uncertainties for different intervals of the tests are presented in Table II.

Table II. Hydrogen and Oxygen Standards and Uncertainties

Period of Test (days)	0-29	1-10	15-63	0-29	1-10	15-63
Standard	100 ppm H ₂	1000 ppm H ₂	10,000 ppm H ₂	17% O ₂	16% O ₂	15% O ₂
# analyses	5	6	10	7	6	11
Average	102	1010	10,118	16.9	16.2	14.7
Standard deviation	3.5	20.0	297.8	0.3	0.3	0.1
% standard deviation	3.4	2.0	2.9	1.7	1.8	0.7

The relevant design information for the DEB and VEI getter materials are presented in Table III. The two types of getters were packaged slightly differently from each other. The DEB getter was wrapped in a KimWipe[®] and then surrounded by a wire screen. The ends of the screen were plugged with rubber stoppers. The VEI getter had an additional layer of molecular sieves to help scavenge water that may be produced by the recombination reaction. This layered assembly was the same configuration employed in previous laboratory testing.[1] Relevant specifications for these getter assemblies are presented in Table IV.

Table III. Design Information

	Total mol H ₂ Generated in 60 days	Mass of DEB Needed to Absorb 2x of Maximum H ₂ Produced (kg)	Mass of VEI Needed to Absorb 2x of Maximum H ₂ Produced (kg)	Mass of Molecular Sieve Accompanying VEI (kg)
7 drums in TRUPACT-II	3.36	0.62	1.14	1.03
scaled drum (82.6 L) in belljar	1.34	0.25	0.46	0.41
			DEB Specifications	VEI Specifications
stoichiometry	fraction DEB/(g/mol of DEB)		2.69E-03	—
capacity	mol H ₂ /mol DEB		4	—
	mol H ₂ /g DEB		1.08E-02	—
	mol H ₂ /kg DEB		10.78	5.88

Table IV. Specifications for Getter Assemblies, as Built

	DEB Assembly	VEI Assembly	Molecular Sieve (part of VEI assembly)
Specifications	Honeywell FM&T Lot x229	27TS138	Acros Tupe 13z, 8-12 mesh, Lot A019863401
Mass of material (g) in “inner” cylinder	250	460	0
Length of inner cylinder (inches)	4.5	7.06	NA
Diameter of inner cylinder (inches)	2.5	2.5	NA
Mass of molecular sieve in outer annulus	NA	NA	410
Length of outer annulus (inches)	NA	NA	7.25
Diameter of outer annulus (inches)	NA	NA	3.5

Hydrogen Sorption Using Nuclear Magnetic Resonance Spectroscopy

In the presence of a strong magnetic field the energies of the nuclei of certain elements are split into two or more quantized levels. Transitions among the resulting magnetically induced energy levels can be brought about by absorption of electromagnetic radiation of suitable frequency, just as electronic transitions are caused by the absorption of ultraviolet or visible radiation. Neighboring similar atoms influence the energies of these transitions. Thus nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that allows one to identify the electronic ‘neighborhood’ that atoms reside within and to quantify the number of atoms in that electronic ‘neighborhood’.

Fortuitously, the symmetric structure of DEB makes it possible to easily identify each of the hydrogens in the proton NMR spectrum. Fig. 1a is a schematic diagram of the hydrogens on the unreacted DEB molecule and labels those that are in similar environments with the same numbers. Thus, in the NMR spectrum, there are four types of hydrogens—four **1**'s, four **2**'s, four **3**'s, and two **4**'s.

The peaks in the NMR spectrum are assigned according to known structure libraries, spiking compounds of known composition, and experience. The NMR spectrum in Fig. 1b is a partial spectrum of the unreacted DEB in which the peaks have been assigned numbers connecting them to the molecular drawing in Fig. 1. The **1**'s show up as a series of peaks between 7.4 and 7.5 ppm. The four **3**'s show up as a nice strong single peak at about 7.33 ppm. And the **2**'s and **4**'s are part of the structure in the 7.0 ppm region. The peak at 7.1 ppm and some of the structure in the 7.0 ppm region are from the toluene-d8 that was spiked into the sample for instrument calibration. Fortunately, the **2**'s and **4**'s are not important with regards to the reactions that the getter undergoes during hydrogen uptake (hydrogenation).

The exact reaction mechanism for catalytic hydrogenation of the triple bonds remains to be determined for DEB. Fig. 1c represents the range of some possible outcomes. If only one of the alkyne bonds is broken and a hydrogen is added to each of the carbons involved, the hydrogens of type **5** would result. Such a change would affect the original neighboring **1**'s and **3**'s to give what we have called **7**'s and **9**'s; all three of these changes would become quite obvious in the proton NMR spectrum. If however, the alkynes are completely hydrogenated to alkane bonds then there will be four new hydrogens added to the structure, designated **6**'s in Fig. 1c. Then corresponding original **1**'s and **3**'s would be unique and are labeled with **8**'s and **10**'s in Fig. 1c. Finally, it would be possible to definitively detect any loss of

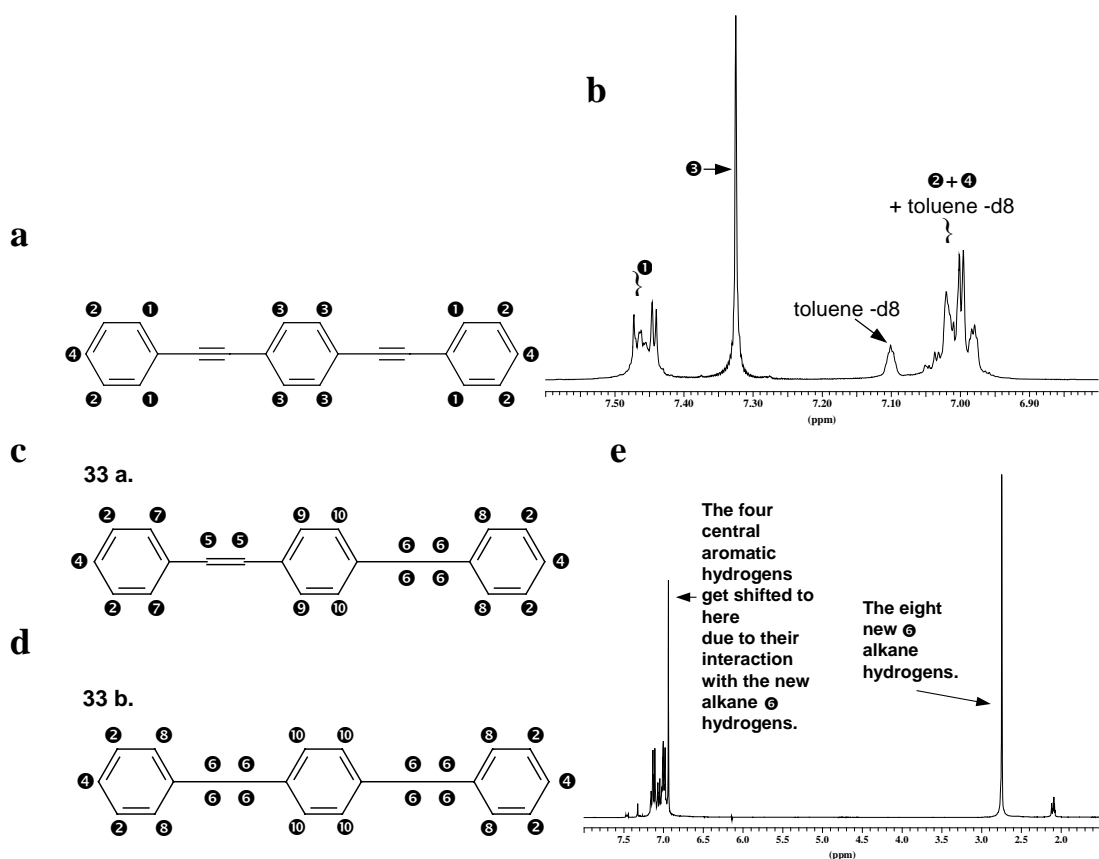


Fig. 1. (a) Schematic diagram of the NMR equivalent hydrogen atoms on the unreacted DEB getter. (b) NMR spectral assignment of the hydrogens on the DEB as diagramed in 1a. (c) and (d) Schematic diagram of the potential NMR equivalent hydrogen atoms on the reacted DEB getter. (e) NMR spectrum with assigned peaks of DEB getter that has been saturated with hydrogen.

aromaticity in any of the rings if any of that should occur (such reactions are very hard to obtain under normal reaction conditions such as are present in these tests).

A preliminary spectrum to test this thinking was obtained with a sample of DEB that had been exposed to a saturating level of hydrogen. The results are shown in Fig. 1e. The analysis of this particular sample indicates that virtually all of the alkyne bonds were completely hydrogenated. Thus all of the 1's and 3's of Fig. 1a were converted to 8's and 10's, Fig. 1d. No intermediate structures are indicated and no involvement of the aromatic rings was observed. Furthermore, by integrating the areas under the peaks it is possible to state that 95% of the hydrogen capture capacity of this sample was consumed. The amount of hydrogen captured can be calculated from the pressure changes over the course of the experiments.

RESULTS AND DISCUSSION

Hydrogen Generation Rate

Table V summarizes the rate at which hydrogen was introduced into the drums of each of the three tests. The target hydrogen generation rate of $2.60\text{E}-07$ mol H_2 /second (0.35 cc H_2 /minute) was achieved in all three tests.

Table V. Summary of Hydrogen Introduced into Drums of DEB and VEI Tests

Mean Rate, All Tests	2 σ , DEB Test	2 σ , VEI Test	2 σ , Duplicate DEB Test
2.60E-07 mol H ₂ /second	2.97E-08	5.94E-08	1.49E-08
1.56E-05 mol H ₂ /minute	1.78E-06	3.55E-06	8.89E-07
0.35 cc H ₂ /minute	0.04	0.08	0.02

Temperature-Pressure History and Integrity of Test System

Tables VI, VII, and VIII present correlation coefficients for temperatures (internal temperature of belljar, exterior surface temperature of belljar, ambient temperature) and pressures (internal pressure of belljar, and ambient pressure) that were measured and recorded by the data logging system during the DEB test, the replicate DEB test, and the VEI test, respectively. A correlation coefficient is a number between -1 and 1 that measures the degree to which two variables are linearly related. If there is perfect linear relationship with positive (or negative) slope between the two variables, the correlation coefficient is 1 (or -1). A correlation coefficient of 0 means there is no linear relationship between the variables. Recorded data (2.4 to 3.2, 31.1 to 32.2, and 49.9 to 51.2 days) exhibits gaps due to short-term failures in the automated data logging system. The data gaps total 3.2 days and comprise 5% of the total duration of the test. Detailed charts depicting the temperature and pressure history of the DEB test, the replicate DEB test, and the VEI test are reported elsewhere.[1] Several relationships are evident upon examination of Tables VI, VII, and VIII.

1. In each of the three tests, the temperature inside the belljar and the temperature of the exterior surface of the belljar are within 1°C of each other. Since the uncertainty in temperature measurement is $\pm 1^\circ\text{C}$, these two temperatures are essentially equal for each test.
2. In each of the three tests, ambient temperature was 2 to 5°C greater than both belljar temperatures. The placement of the thermocouple in the test room accounted for approximately 2°C of this difference. The remainder of this temperature difference is due to a lag between the ambient temperature and the temperature in the belljar. The belljars were not separately heated or cooled. Instead, the ambient temperature in the test room controlled the temperature of these test vessels. Since the belljar contains a large thermal mass of stainless steel, belljar temperatures lagged behind ambient test room temperature. Changes in test room temperature were due to diurnal changes of approximately 2°C and passage of weather fronts that led to temperature changes of up to 2°C.
3. In each of the three tests, internal and external belljar temperatures are strongly correlated (correlation coefficients of 0.96 to 1.00). The weaker correlation between belljar temperatures and ambient temperature (correlation coefficients of 0.89 to 0.97) are due to the temperature lag between temperature in the test room and in the belljar.
4. For both DEB tests and for the second half of the VEI test, temperature and pressure within the belljar are strongly correlated (correlation coefficients ranging from 0.84 to 1.00). In the first half of the VEI test, temperature and pressure within the belljar were not as strongly correlated (correlation coefficients 0.70 to 0.77). From these relationships, we conclude that pressure cycles in each of the three tests are the result of temperature cycles.
5. In each of the three tests, pressure within the belljar does not correlate with ambient pressure (correlation coefficients range from -0.58 to 0.61). In conjunction with the previous observation, we take these data as evidence that the test vessel was a closed system, effectively isolated from the atmosphere of the test room.

Table VI. Correlation Coefficients for DEB Test

Data Type	Correlation Coefficient in Specified Interval			
	0-2.4 days	3.2 to 31.1 days	32.2 to 49.9 days	51.2 to 63.9 days
internal belljar temperature - belljar exterior surface temperature	0.96	1.00	1.00	1.00
internal belljar temperature - ambient temperature	0.89	0.97	0.95	0.95
internal belljar temperature - internal belljar pressure	0.99	0.84	0.89	0.98
internal belljar pressure - ambient pressure	-0.55	-0.20	0.40	0.28

Table VII. Correlation Coefficients for Replicate DEB Test

Data Type	Correlation Coefficient in Specified Interval			
	0-2.4 days	3.2 to 31.1 days	32.2 to 49.9 days	51.2 to 63.9 days
internal belljar temperature - belljar exterior surface temperature	0.96	1.00	0.99	1.00
internal belljar temperature - ambient temperature	0.94	0.97	0.95	0.96
internal belljar temperature - internal belljar pressure	0.98	1.00	0.98	0.98
internal belljar pressure - ambient pressure	-0.58	-0.18	0.18	0.34

Table VIII. Correlation Coefficients for VEI Test

Data Type	Correlation Coefficient in Specified Interval			
	0-2.4 days	3.2 to 31.1 days	32.2 to 49.9 days	51.2 to 63.9 days
internal belljar temperature - belljar exterior surface temperature	0.96	1.00	0.99	1.00
internal belljar temperature - ambient temperature	0.93	0.97	0.94	0.95
internal belljar temperature - internal belljar pressure	0.77	0.70	0.89	0.96
internal belljar pressure - ambient pressure	-0.31	-0.05	0.35	0.61

Hydrogen Evolution

Analytical results for gas samples from the belljar headspace of the DEB test is presented in Fig. 2. Analytical results for gas samples from the drum headspace of the DEB test and the belljar and drum headspace of the replicate DEB test and the VEI test are presented elsewhere.[1] Fig. 2 plots

concentration of hydrogen (millimole) and oxygen (mole) as measured in the gas samples as well as the amount of hydrogen (mole) injected into the drum and oxygen (mole) consumed during the test. The test results are presented in units of moles, instead of % oxygen and parts per million (ppm) hydrogen, to facilitate mass balance and promote understanding of reaction mechanism.

In all tests, the concentration of hydrogen in the headspace of belljars containing DEB and VEI did not exceed 5 volume percent (vol%). The amount of hydrogen within the headspace of each of the belljars remained approximately 2 orders-of-magnitude below the 5 vol% threshold for the duration of the test. After the initial 15 to 20 days of the DEB tests (*i.e.*, 25 to 30% into each of the tests), the hydrogen concentration plateaued at 0.04 vol % in the DEB test and at 0.02 vol% in the duplicate DEB test. After the initial 15 to 20 days of the VEI test, the hydrogen concentration plateaued at 0.01 vol %.

In all tests, the concentration of hydrogen in the drums also did not exceed 5 vol%. Hydrogen concentrations in the drums displayed greater variability than observed in the belljars. The amount of hydrogen within the drums in the tests containing DEB remained approximately 1 order-of-magnitude below the 5 vol% threshold. After the initial 15 to 20 days of the DEB tests, the hydrogen concentration plateaued at approximately 0.4 vol% in the DEB test and at 0.2 vol% in the duplicate DEB test. Hydrogen concentrations in the duplicate DEB test also display a maxima of 0.25 vol% at day 15 and a minima of 0.12 vol% at day 30. The amount of hydrogen within the drum in the VEI test plateaued at 2.5 vol % in the second half of the 60 day test. Elevated hydrogen concentrations approaching 5 vol% were observed at days 15 and 55 of this test.

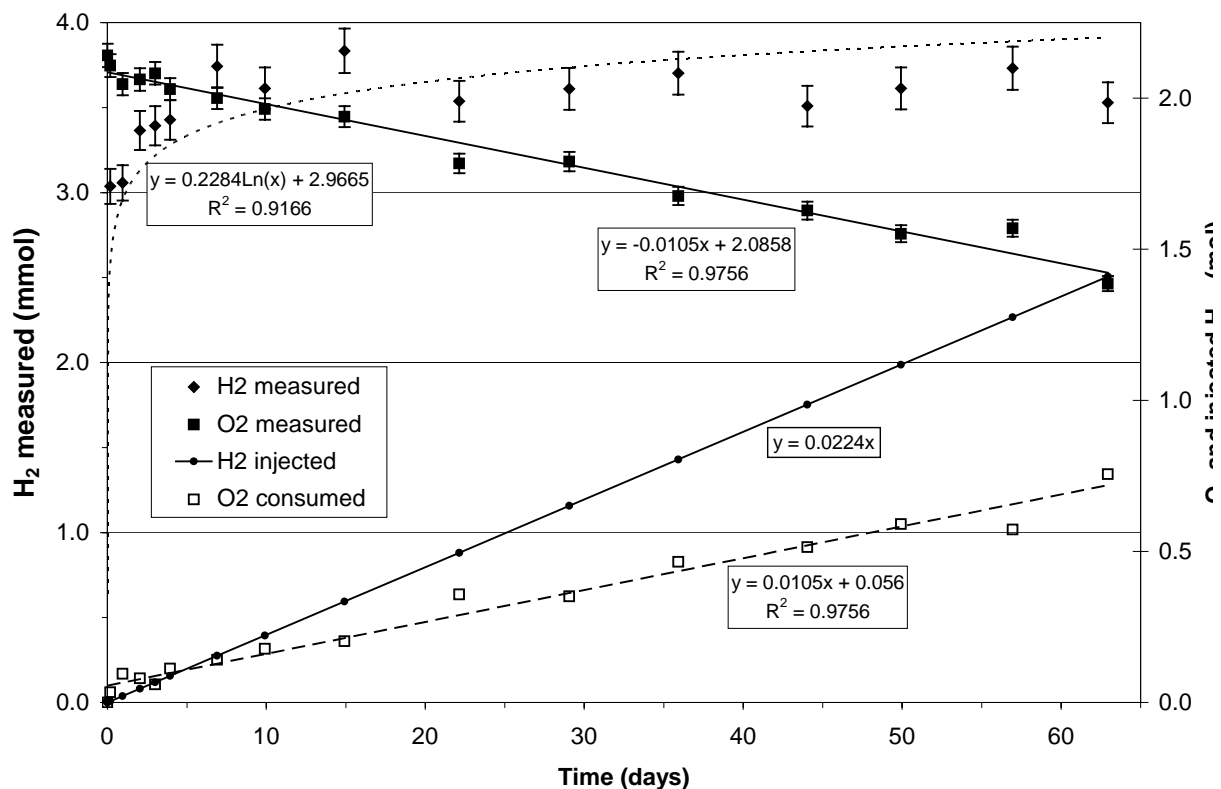


Fig. 2. Gas evolution as a function of time for ICV (headspace) of belljar containing DEB. Millimoles of hydrogen measured in this headspace are plotted against axis on left, moles of hydrogen injected into test vessel and moles of oxygen measured/consumed in belljar headspace are plotted against axis on right. Error bars depict uncertainties per Table V. If no error bars are present, then uncertainty is smaller than size of symbol. A logarithmic curve fit has been applied to the measured hydrogen data whereas a linear fit has been applied to the other data sets (measured and consumed oxygen). Equations and R^2 values for each of the curve fits are displayed next to the respective curves. For the volume of the belljar headspace, 0.5 mol hydrogen yields 5 vol% hydrogen.

In addition, the following relationships are also evident:

1. Oxygen is depleted in the drum and in the belljar of both DEB and VEI tests. The rate of oxygen depletion is linear, consistent with a zeroth order kinetic rate law. Linear fits of the data yield correlation coefficients ranging from 0.74 to 0.98.
2. The rate of hydrogen buildup in the belljar headspace containing DEB is logarithmic (correlation coefficients of 0.97 in the primary test and 0.73 in the replicate, see Fig. 2).
3. The rate of hydrogen buildup in the belljar headspace containing VEI is not approximated by a simple curve fit. An attempted logarithmic fit yields a correlation coefficient of 0.32.

In the belljar headspace of the DEB test, the rate of oxygen consumption is proportional to the rate of hydrogen introduced into the test. The proportionality approaches a ratio of 0.5 (Fig. 2), a value expected with the catalytic recombination of hydrogen with oxygen to form water. The relative ratio of oxygen consumption to the rate of hydrogen introduced into the duplicate DEB test is only 1/3 of that expected for catalytic recombination. Similar relationships are observed for the drums in the tests containing DEB. The ratio of oxygen consumption to hydrogen production in the VEI test is also only 1/3 of that expected for catalytic recombination.

Liquid water was condensed on the base of the belljar and on the drum of the DEB test. In addition, the belljar emitted an audible hiss when the lines were disconnected. In both DEB tests, rust and corrosion were present on the drum welds, bottom of drum, by the drum filter, and on the rim of the bung. These observations are consistent with consumption of oxygen and exposure of the drum and belljar to water vapor. No free water or drum corrosion was noted in the VEI test, probably because the molecular sieves contained in the getter assembly absorbed free water. In combination with the analytical data, these observations indicate that catalytic recombination was the predominant mechanism for hydrogen consumption in the DEB test. Catalytic recombination was also important in the replicate DEB test and in the VEI test.

Fig. 3 illustrates the relationships between temperature and the continuously measured hydrogen concentration in the drums of the DEB test and the VEI test. Also plotted for comparison are results of the hydrogen analyses using gas chromatography as well as the correlation coefficients between temperature and hydrogen concentration that were measured and recorded by the data logging system. Several relationships are evident in Fig. 3. In the DEB test, the results of the hydrogen analyses made with the Meggitt sensors and the gas chromatograph agree very well. One prominent outlier is on day 14.9. The reason for this discrepancy in the data is not known. During the first 4.2 days of the DEB test, the hydrogen concentration increases from 0% to approximately 0.11%. After approximately 4.2 days, the mean hydrogen concentration plateaus and cycles in positive correlation with temperature. We take this observation as evidence that the first 4.2 days of the DEB test represent a period of time in which the drum-belljar system is reaching steady state. After 4.2 days, hydrogen input into the drum, diffusion of hydrogen from the drum through the bung filter into the belljar, and consumption of hydrogen by getter material within the belljar are at steady state. From this time forward, hydrogen concentration in the drum is controlled by temperature. Diurnal temperature cycles as well as broad temperature patterns are mirrored in the hydrogen data of both DEB tests.

The hydrogen data in the replicate DEB test displays a greater disparity between hydrogen analyses with the Meggitt hydrogen sensors and the gas chromatograph. This discrepancy is likely due to the very low levels of hydrogen present in this test. The detection limit of the Meggitt sensor is approximately 0.1%, whereas hydrogen measured during the course of the replicate test never exceeded this threshold. The different levels of hydrogen in these two tests may be due to physical heterogeneities present in test vessels of this complexity. Small differences in packaging and handling of the DEB, in accumulation of H₂O during catalytic recombination, and in diffusivity of the bung filters may have all contributed. However, it must be noted that exceedingly small levels of hydrogen are present in drums of both tests, 0.17% in the DEB test and 0.10% in the replicate test. In evaluating these analytical data, it is not surprising that discrepancies exist. Comparing values of small numbers can lead to large apparent differences.

In the VEI test, the results of the hydrogen analyses made in the drum with the Meggitt sensors and with the gas chromatograph agree exceedingly well (Fig. 3). One prominent outlier is on day 16.9. The reason for this discrepancy in the data is not known. The percent levels of hydrogen present in the drum of the VEI test are well within the range of accuracy of the Meggitt analyzer, hence the excellent agreement in the analytical results of the two methods. The hydrogen data in the VEI test do not correlate with temperature as observed in the DEB tests. The reasons for this phenomenon, for the percent levels of hydrogen in the drum compared to the small fraction of a percent of hydrogen in the drums of the DEB tests, and for the cycling observed in the hydrogen within the drum of the VEI test are unknown. One possibility is that the layered packaging of VEI getter within the molecular sieve and the accumulation of H₂O in the sieve affect the dynamics of hydrogen diffusion between the drum and belljar ICV.

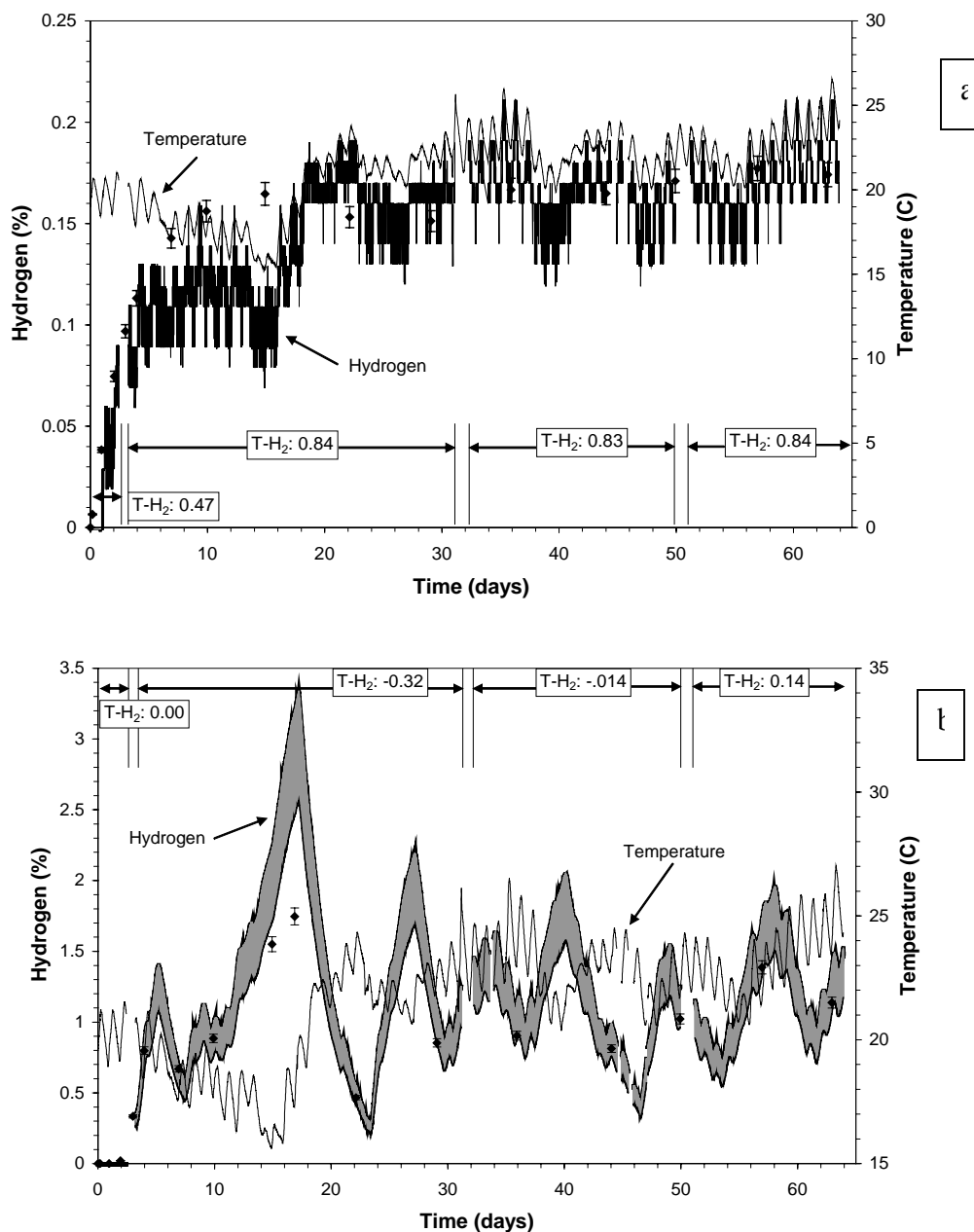


Fig. 3. (a) Hydrogen (in units of %, left axis) in drum of DEB test (thick line) compared to system temperature (°C on right axis) in test vessel (thin line). Also plotted are the hydrogen analyses obtained with gas chromatography (diamonds). Correlation coefficients between temperature and the continuously measured hydrogen concentration are provided in boxes labeled T-H₂ for intervals of 0 to 2.4, 3.2 to 31.1, 32.2 to 49.9, and 51.2 to 63.9 days. Uncertainty in the hydrogen data that was continuously measured by the Meggitt sensors is $\pm 6\%$. (b) Hydrogen in drum of VEI test (2 lines bounding the shading) compared to system temperature (thin line). Correlation coefficients between temperature and the continuously measured hydrogen concentration are provided in boxes labeled T-H₂ for intervals of 0 to 2.4, 3.2 to 31.1, 32.2 to 49.9, and 51.2 to 63.9 days. Accuracy of Meggitt sensors drifted during course of the test. Final calibration of the sensors indicate $\leq 30\%$ uncertainty in the continuously measured hydrogen data, as indicated by shaded region between black lines.

NMR Results

NMR spectra (Fig. 4) were taken of both getters: (1) before any exposure to hydrogen, (2) at the completion of the scaled experiments, and (3) fully saturated with hydrogen (in the INL mini-test apparatus). The spectra of the control getters and that of the getters after testing are identical. This would indicate that all of the hydrogen gettering that took place was a result of recombination reactions.

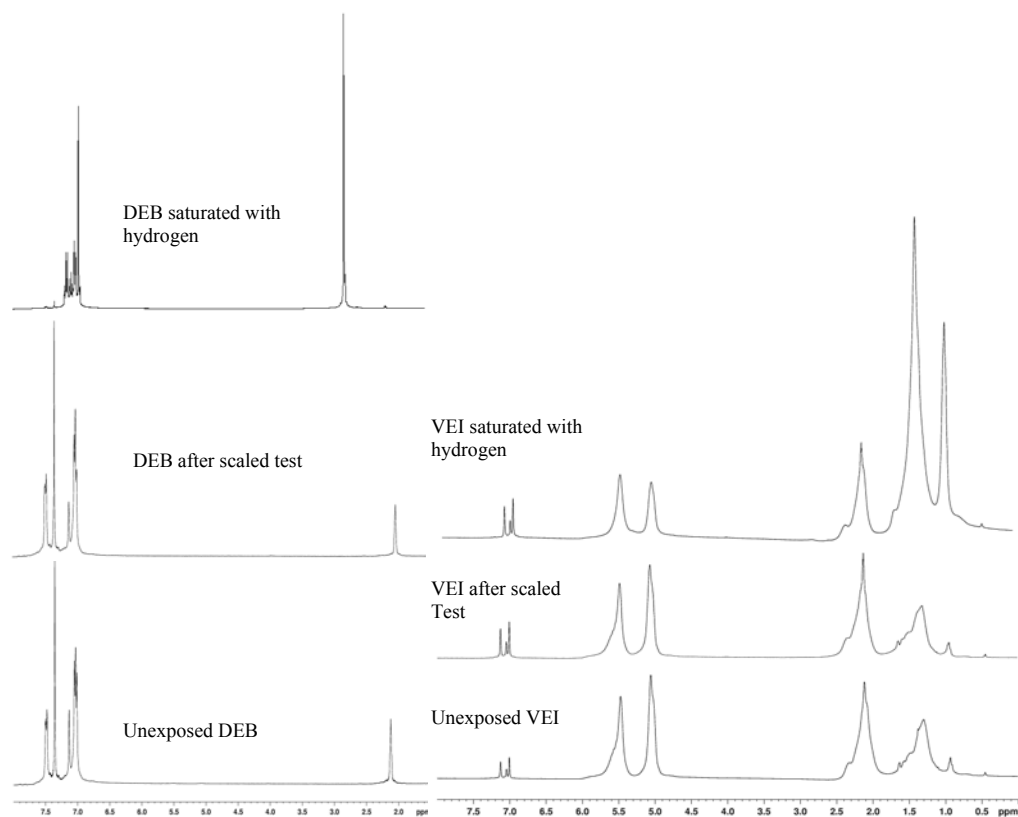


Fig. 4. NMR spectra from unexposed getters, getters used in this set of tests, and samples of the two getters after they were saturated with hydrogen. No chemical changes in the getters were observed from these experiments. They show that all of the hydrogen removal under the experimental conditions was due to recombination of the hydrogen with the oxygen in the bell jars.

During the process of calibrating the NMR spectra for DEB, large differences were observed between two rates of hydrogen introduction. When the hydrogen is added suddenly, a much smaller quantity of hydrogen is captured compared with what is theoretically possible (based upon the 4 moles of hydrogen to 1 mole of DEB). Yields of about 63% were observed. However, when the hydrogen was allowed to bleed onto the getter bed at much slower rates, conversions of 90+% were observed. Thus it is important that the getter encounters the hydrogen at slower rates in order to maximize its hydrogen capacity.

We have had a hard time determining exactly what happens when the getter is exposed to the hydrogen all at once. Observations at LANL, Savannah River, and INL indicate that when the getter materials are added to the sample chamber they are separate granules. However, after the sudden exposure to hydrogen, DEB granules appear to be melted or sintered together to form a rigid structure. This change possibly

alters the morphology of the granules. The heat generated by the reaction of the getter to the high rate of addition could melt micro-areas of the material. This could produce DEB rich areas that are catalyst poor, resulting in portions of the DEB not reacting with the hydrogen. The result would be lower conversion rates such as those observed. Different lots and different preparations of the getter (such as vacuum drying) did not improve the conversion rates for runs made with high hydrogen feedstreams.

CONCLUSIONS

The overall goal of this program was to investigate the potential for using hydrogen getter materials in TRUPACT containers to prevent the build up of hydrogen to a dangerous level. Both DEB and VEI getters were tested in scaled replicas of TRUPACT-II containers. The tests were run with an atmosphere of air for 63.9 days at ambient temperature (15 –27°C) and a scaled hydrogen generation rate of 2.60E –07 moles per second (0.35 cc/min). In addition, benchtop tests were performed to determine at a more detailed level the optimal conditions that achieved the maximum getter conversion rates. Our conclusions from both benchtop and larger scale testing are:

1. Both DEB and VEI getters have the needed rate of conversion
2. Both getters can remove hydrogen to >90% of theoretic calculated values
3. The capacity of the getters will perform satisfactorily if the rate of introduction of the hydrogen to the getter happens slowly over the expected lifetime of the getter
4. The getter as received by the producer is useable and no other preconditioning is needed.
5. Hydrogen was successfully “gettered” by both DEB and VEI getters. Hydrogen concentrations remained below 5 vol% (in air) for the duration of the tests.
6. Catalytic reaction of hydrogen with carbon triple or double bonds in the getter materials did not take place. Instead, catalytic recombination was the predominant gettering mechanism in both getter materials as evidenced by (1) consumption of oxygen in the belljars; (2) production of free water in the belljars; and (3) absence of chemical changes in both getter materials as shown by NMR spectra.
7. The amount of oxygen in the bell jar was enough to react with all of the hydrogen through the recombination mechanism over the experimental time period. This result suggests that the catalyst/carbon mixture may be all that is needed to safely remove the hydrogen in the shipping containers under current DOE and DOT requirements.

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REFERENCES

1. Stone, Mark, Benson, Michael, Orme, Christopher, Luther, Thomas, Peterson, Eric, Kaszuba, John, Haga, Marc, Hollis, Kirk, Mroz, Eugene, 2005, Improved Hydrogen Gas Getters for TRU Waste—Final Report, INL/EXT-05-00805 and LANL LA-UR-05-7316, 84 p.
2. Stone, Mark, Orme, Christopher, Peterson, Eric, Kaszuba, John, Mroz, Eugene, and Haga, Marc, 2003, Gas permeation testing results from the Mixed Waste Focus Area improved hydrogen getter program: 13th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 26-30, paper #190.
3. Kaszuba, John P., Peterson, Eric, Mroz, Eugene, Stone, Mark, and Haga, Marc, 2004, Development of hydrogen gas getters for TRU waste: Proceedings of the Waste Management 2004 Conference, Tucson, AZ, February 27 - March 3, Paper #4237.
4. Stone, Mark, Orme, Christopher, Peterson, Eric, Kaszuba, John, Mroz, Eugene, and Haga, Marc, 2005, Gas permeation testing results from the Mixed Waste Focus Area improved hydrogen getter program: Separation Science and Technology, v. 40, no. 1-3, p. 419-431.
5. Sheppard, T. J., Gillion, L. R. , and Smith, H. M., 1989, Organic getter materials for the removal of hydrogen and its isotopes: Fourth International Conference on the Effects of Hydrogen on the Behavior of Materials, Moran, Wyoming, September 12–15.
6. Smith, H. M., and Sheppard, T. J., 1990, Hydrogen-tritium getters and their applications: Radioluminescent Lighting Technology Transfer Conference, Annapolis, Maryland, September 25–26.
7. American Society of Mechanical Engineers, July 2002a, Technical Peer Review Report—Enhanced Polymer Hydrogen Gas Getter Material: ASME/CRTD-RP-02-41, ASME International, Columbia, Maryland.
8. American Society of Mechanical Engineers, July 2002b, Technical Peer Review Report—Polymer Encapsulation of Hydrogen Gas Getter: ASME/CRTD-RP-02-42, ASME International, Columbia, Maryland.