POLYMER-BASED HYDROGEN GETTERS FOR TRANSPORT PACKAGINGS

Tim Shepodd[*], Paul McConnell[**], Ron Livingston[***], Jon Duffey[***]
[*]Sandia National Laboratories
Livermore, California 94551-9402 USA
[**]Sandia National Laboratories[1]
Albuquerque, New Mexico 87185-0716 USA
[***]Westinghouse Savannah River Company, Savannah River Technology Center
Aiken, South Carolina 29808 USA

ABSTRACT

Polymer-based hydrogen getters are described and their effectiveness for reducing hydrogen levels in radioactive materials (RAM) packagings is demonstrated. These Sandia National Laboratories patented getters have been characterized, in United States Department of Energy Office of Environmental Management programs (National Transportation Program and TRU & Mixed Waste Focus Area), for hydrogen mitigation under conditions existing in RAM packagings.

The decomposition of radioactive waste produces non-radioactive gaseous by-products, including hydrogen. Additional gases and vapors (getter "poisons") may be present in sealed waste containers. The accumulation of hydrogen within waste packages presents a safety hazard. Regulatory limits on the hydrogen concentration in RAM packagings may require costly repackaging (and more shipments) or waste treatment unless hydrogen accumulation can be mitigated. The use of hydrogen getters is a promising mitigation technology.

The Sandia getters consist of a mixture of organic polymers containing carbon-carbon double bonds and a palladium or platinum catalyst on a carbon support. In the absence of oxygen, hydrogen is removed by reaction with the carbon-carbon double bonds (i.e., hydrogenation). When oxygen is present, the polymer-based getter functions primarily as a recombination catalyst until the oxygen is consumed, after which the hydrogenation mechanism takes over. The polymer-based getters have demonstrated favorable hydrogen gettering characteristics relative to the requirements for specific packaging applications, such as the DDF-1 packages at the Savannah River Site and the TRUPACT-II for the Waste Isolation Pilot Plant.

The polymer-based getters are non-pyrophoric, recombine H_2 and O_2 regardless of capacity, require no activation, remove hydrogen in a variety of atmospheres, are compatible with a wide range of materials, have demonstrated resistance to many "poisons" (e.g., carbon tetrachloride) and radiation, are effective over a wide temperature range, and are commercially available at relatively low cost. The getters have been shown to perform effectively in terms of Nuclear Regulatory Commission criteria which include capacity, pressure, "poisons", reversibility, temperature, humidity, and thermal output.

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[1] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE- ACO4-94AL85000.

SANDIA NATIONAL LABORATORIES POLYMER GETTERS

Sandia National Laboratories (SNL) has developed and patented a family of polymer-based hydrogen getters useful for scavenging unwanted hydrogen for a variety of industrial applications [1-6]. The polymer hydrogen getters are used in oil production, heat exchangers (e.g., in coal-fired power plants), sealed electric devices, and vacuum insulation panels -- all applications where hydrogen represents a safety hazard or significant loss of process efficiency. Generically, the getters have excellent resistance, with demonstrated performance in the presence of oils, oxygen, and boiling water. In many instances, they possess excellent temperature resistance (functional from -30°C to 175°C) and have a low vapor pressure. They do not require any active circulation as diffusion and convection will cause enough gas motion to eliminate hydrogen safety concerns. One major improvement in the development of these getters is that the formulation prevents the catalyst from being wetted by water. This is a fundamental property of the polymer-based getter formulation; engineered vapor barriers are not required. (DEB-type getters are not recommended for liquid water or steam applications because of facile steam distillation of DEB and its fully hydrogenated product, and because wet catalyst can become deactivated.) They are not subject to the sublimation problems inherent to DEB getters. The getters are available in a variety of physical forms for versatile deployment (powder, pellets, monoliths, spray coatings) and can be produced in cost-effective, commercial quantities.[2]

In addition to these commercial formulations, Sandia has developed hydrogen getters specifically tailored (chemically formulated) to the needs for shipments of radioactive material and, in particular, transport of transuranic wastes. For application in TRUPACT-II packages, these getters may allow waste to be moved safely while in excess of 1394 standard liters of hydrogen gas is generated over the 60-day maximum shipment period.

The SNL polymer-based getters consist of an unsaturated rubbery polymer dispersed on a precious metal catalyst. Precise formulation with proprietary additives yields an inherent poison resistance and a hydrogen uptake rate sufficient to meet extreme environments. The commercially available VIP getter, for instance, is a precious metal composite of organic polymers such as an isobutylene-butene copolymer, polybutadiene, styrene-butadiene copolymer, carbon, and poly(1,2-dihydro-2,2,4-trimethylquinoline), which is an antioxidant. Gettering rates depend on the mobility of the polymer molecules to the catalyst, so the gettering rate slows as the temperature drops. The polymer must have sufficient mobility to react at the required cold conditions (-29°C for TRUPACT-II); yet, the polymers must not be overly reactive during the exothermic reaction at the hottest temperature (71°C for TRUPACT-II).

Polymer-based getters work on the principle of catalytic hydrogen addition to carbon-carbon multiple bonds.

$$H_2 + (-HC{=}CH-)_n \rightarrow (-H_2C-CH_2-)_n \qquad \text{[hydrogenation]}$$

When O_2 is present, H_2 and O_2 are catalytically recombined to form water.

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[2] Vacuum Energy, Inc., Cleveland Ohio, licenses the Sandia National Laboratories-patented polymer getters.

$$2H_2 + O_2 \rightarrow 2H_2O \quad \text{[recombination]}$$

Gettering capacity depends on the number of double and/or triple carbon-carbon bonds. Polymer based getters do not require a pressure threshold of hydrogen to be activated. When exposed to hydrogen, the carbon bonds in the polymer hydrogenate, thus irreversibly scavenging hydrogen. Under static conditions, hydrogen uptake is typically limited by the rate of diffusion to the getter. Typical hydrogenation capacities are 75 to 200 std cc H_2 per g of getter. The typical getter has a capacity of approximately 100 std cc/g. The catalytic recombination reaction preserves gettering capacity (The H_2 is consumed producing H_2O) and also removes oxygen in a controlled fashion so an undesired hydrogen/oxygen ignition/explosion cannot occur. The getter is designed to keep the hydrogen below explosive limits at all times regardless of oxygen depletion. The rate of gettering slows as the temperature drops, so the lowest temperatures are the most challenging.

The polymer-based getters are formulated with additives to produce the desired poison resistance and provide sufficient hydrogen uptake rates under the extreme TRUPACT-II environments. Sandia National Laboratories is currently designing for poison concentrations of up to 1000 ppm (acid gases, CO, sulfides, halogenated hydrocarbons). Carbon tetrachloride (CCl_4) has been used as a representative screening poison since it exists in some drums destined for TRUPACT-II shipment and is one of the more aggressive poisons known for these polymer getters. Most non-halogenated organic solvent vapors have little or no effect on the polymer-based getters. Some functionalities (ketone/aldehyde) can be reduced or partially reduced in the presence of hydrogen, but this does not affect the hydrogen gettering reactions. Chlorinated hydrocarbons can have a dramatic, irreversible effect on the ability of hydrogen getters to function, especially at high solvent concentrations. Polymer-based getters are to some extent reversibly poisoned by reactive molecules, which interfere with the noble metal hydrogenation catalysts. Free radical initiators (e.g., O_2, SO_2, NO, NO_2), which can polymerize or oxidize (deactivate) the carbon-carbon double and triple bonds in a polymer-based getter, can be removed with appropriate inhibitors (scavengers). Carbon monoxide, hydrogen sulfide, ammonia/amines, and other active ligands all slow the hydrogenation reaction.

The polymer-based hydrogen getters are produced as a free-flowing black powder that can be extruded into pellets or other engineered forms for ease of handling. The getter is formulated from readily available commercial precursors. Expected application to RAM packagings would allow the getters to remain non-hazardous materials for disposal and to be recycled for their noble metal content.

THE TRANSPORT PACKAGE APPLICATION FOR GETTERS

Many challenges to hydrogen getters are specific to RAM transport packages [7]: temperature extremes, hydrogen capacity, longevity, irreversibility, material compatibility, radiation exposure, completely passive system required, no gas or free water produced, and in particular for TRUPACT-II, aggressive chemicals within the package ("poisons"). These challenges were considered as a system by SNL by which a getter was developed that meets these challenges for TRUPACT-II application.

Interaction of radiation from TRU elements with the waste matrix being transported in the TRUPACT-II results in decomposition of the waste and production of non-radioactive gaseous by-products. Additional gases and vapors may be present in the sealed TRU waste containers from other sources, such as volatilization of waste content and thermal or biological degradation of waste components. The headspace of TRU wasted drums has been shown to include gases and vapors such as hydrogen, oxygen, carbon dioxide, carbon monoxide, methane, trichloroethylene (TCE), hydrogen chloride, and acetone. The accumulation of hydrogen within the individual waste packages and drums, as well as within the sealed TRUPACT-II inner containment vessel (ICV), presents a safety hazard. The Safety Analysis Report for the TRUPACT-II Shipping Package limits the hydrogen concentration to less than 5% by volume to avoid forming flammable gas mixtures.

A limit of 40 Watts (W) has been placed on the overall radioactive decay energy of the TRUPACT-II contents based on the package's ability to dissipate the decay heat. However, the character of TRU waste matrices and the energy of some radioactive contaminants prevent the container from being loaded to the full 40-W limit because the amount of hydrogen produced could result in flammable gas mixtures. The amount of hydrogen generated is a function of both the waste type and the decay energy; therefore, operating limits for allowable radioactive decay energy in the TRUPACT-II have been established for different waste types. For wastes contaminated with Pu-238, which decays at about 0.5 W/g, the total TRUPACT-II loading may be limited to only 3 W (6 g Pu-238) depending on the waste type and layers of confinement.

The current Savannah River Site waste inventory includes about 7000 drums of Pu-238 contaminated waste, with more than half of these containing greater than 6 g of Pu-238. Needs for technologies to prevent hydrogen accumulation in the TRUPACT-II exist at other sites within the DOE that have high-wattage level wastes. The needs include Pu-238 wastes at LANL, and Am-Cm wastes at Hanford, Idaho National Engineering & Environmental Laboratory, Oak Ridge National Laboratory, and Rocky Flats Environmental Technology Site. Due to current decay energy operating limits, drums of these types of wastes may possibly not be shipped without repackaging to decrease the overall decay energy per drum. This will ultimately result in more shipments and higher transportation costs per waste drum [7].

Extensive testing of the SNL polymer-based getters has been conducted at the Savannah River Technology Center (SRTC) to measure the capacity and rate of gettering under the conditions required for transport package certification. Results of this testing demonstrate that the getter materials have the desired properties for use in the TRUPACT-II and the DDF-1 packages.

SAVANNAH RIVER TECHNOLOGY CENTER PERFORMANCE EVALUATION

Commercial Getter

The hydrogen uptake of the commercial VIP getter under static, constant volume conditions is such that more than 98% of the capacity of this getter is consumed under excess hydrogen within 20 hours. The measured capacity of the VIP getter is 100 std cc/g or 4.46×10^{-3} moles/g. Based on the maximum hydrogen evolution rates for TRUPACT-II, the theoretical required mass of getter, assuming no recombination, would be:

In the drum: 6.2 kg/year/drum
In the ICV: 14 kg/60 days/14 drums

Enhanced Transport Package Getters

The Savannah River Technology Center has characterized the polymer getters for transport package applications including the DDF-1 shipping package [8] and TRUPACT-II. Details of the test methodology and test apparatus are discussed in detail in Reference 8. Characterization of hydrogen getters, and interpretation of test results in terms of specific getter applications, is somewhat dependent upon the test assembly and the variables introduced during testing (gases and poisons present, flow rates, pressure, etc.). No consistent test procedures, such as a consensus standard, for characterizing hydrogen getter performance yet exist, although such a standard would facilitate comparison of different getters and of inter-laboratory data for a given getter. The SNL/SRTC investigators have used a set of characterization criteria possibly acceptable to regulators by which to measure the performance of candidate transport package getters [9]:

Getter Parameter	Evaluation Criterion
Potential Poisons	Potential for poisoning of the getter material from gaseous compounds in the waste.
Compatibility	Chemical compatibility of the getter material with package payloads.
Operating Temperature Range	Potential of the getter to perform over a wide temperature range.
Pressure	Ability of the getter to perform over a wide pressure range.
Reversibility	Potential to desorb hydrogen under storage or shipping conditions.
Material Cost	Cost of engineered form of getter required for package application.
Getter Operational Lifetime (Capacity)	Potential of the getter to absorb hydrogen at a rate that results in less than 5% hydrogen buildup.
Free Liquids	Free liquids generation potential of the getter reaction should not exceed specifications.
Temperature Effect from Getter	The heat of reaction (watts/mole H_2) which determines if a getter temperature effect will be of concern.
Passive Versus Active Getter Systems	The system must be shown to be passive.
Radiation Effects on Getter	Potential effects of radiation on the getter performance must be evaluated.
Structure/Shape	The engineered configuration of the getter system.

The following figures provide schematics of the apparatus and test technique (Figures 1 and 2) and results of testing the polymer-based getter in the presence of potentially damaging “poisons” (Figures 3 and 4).

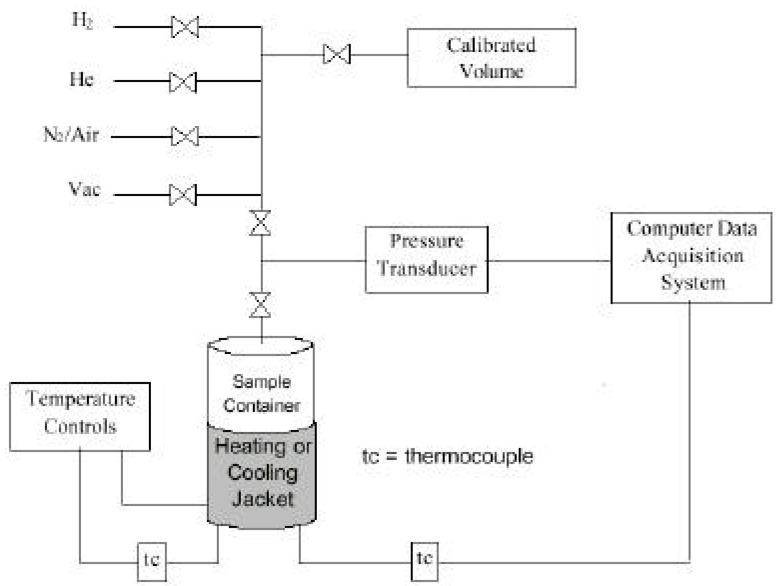

Figure 1. SRTC hydrogen getter test apparatus schematic. Laboratory testing variables include pressure, volume (geometry of vessel and scale), temperature, and atmosphere (including presence of “poisons”).

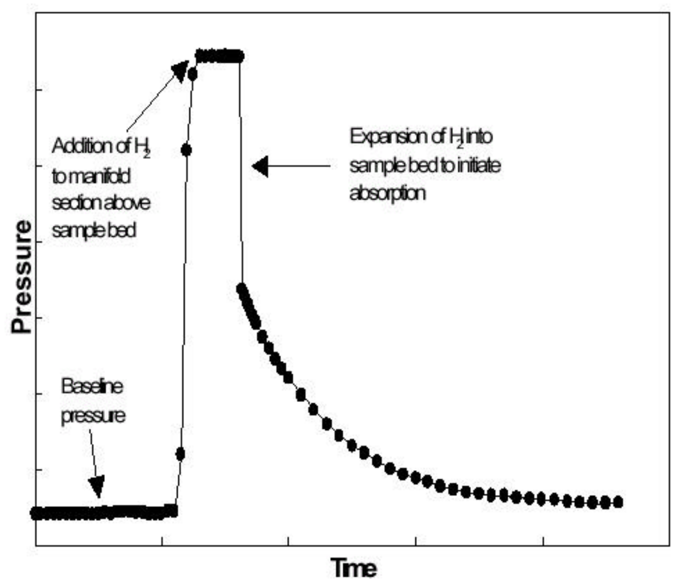

Figure 2. Two essential parameters exist for measurement of getter performance: H_2 absorption rate and getter hydrogen capacity. This figure shows the H_2 pressure drop with time due to absorption by the polymer getter. From such data, getter capacity and absorption rate are derived.

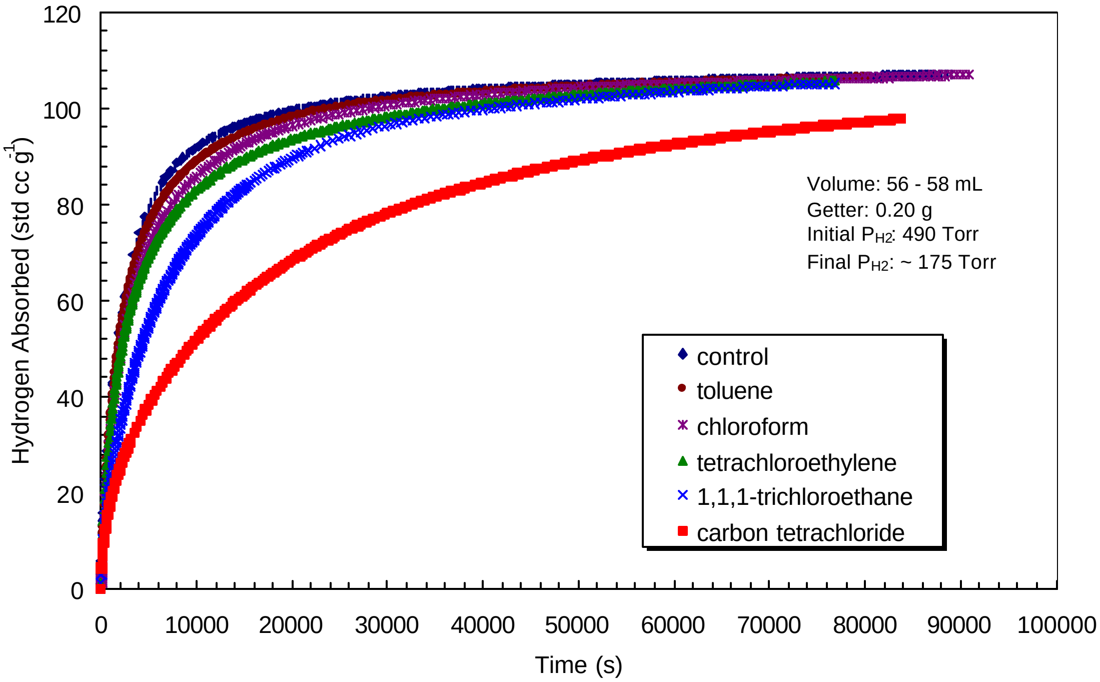

Figure 3. Effect of VOCs (1000 ppm on the absorption of excess hydrogen by SNL polymer getters.

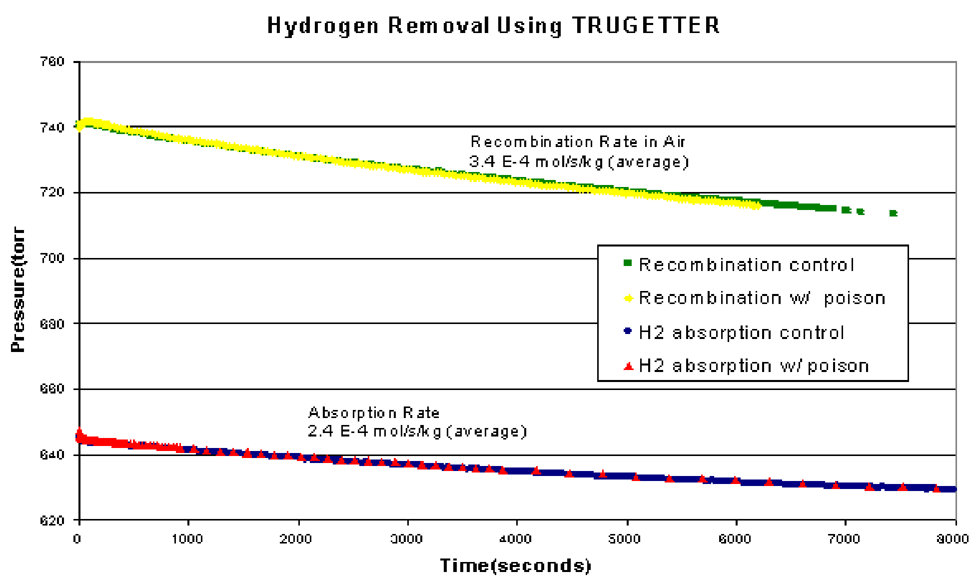

Figure 4. The pressure change in a 5-L vessel as hydrogen is removed by a getter assembly composed of a polymer getter and molecular sieves, with and without the presence of 1000-ppm CCl_4. Since the pressure changes with time, for both absorption and recombination, are nearly identical, this demonstrates that the getter is unaffected by the presence of CCl_4. The test is scaled to provide up to 30 times the headspace volume expected for the full-scale getter assembly loaded in a TRUPACT-II. The 1000-ppm of CCl_4 represents a worst case evaluation and is an expected upper bound for most TRU waste. Other potential poisons have been evaluated in a similar manner and are anticipated to have no impact on performance of the polymer getter assembly.

Essential for application in TRUPACT-II is the performance of the getter in the presence of aggressive chemical gases that may degrade the getter. Tests at SNL indicated that the polymer-based getter has approximately a 50% reduction in H_2 removal rate in the presence of 1500 ppm CCl_4 [10]. Increasing the amount of getter in the package can compensate for this reduction.

SUMMARY

The Sandia National Laboratories polymer-based hydrogen getters, based upon performance evaluations at the Savannah River Technology Center, have been demonstrated to have the hydrogen adsorption rate and hydrogen capacity to maintain hydrogen levels in transport packages below regulatory limits (5%) in terms of proposed evaluation criteria [9]. Furthermore, the polymer-based hydrogen getters have been demonstrated to perform their hydrogen adsorption function in the presence of aggressive volatiles, such as CCl_4. Additional testing of the polymer-based getters shall provide a complete data package on the performance of the getters under simulated transport package environments and, concurrently, provide information for possible modifications to the getter formulations to further enhance their performance.

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