SAND REPORT

SAND2002-8267
Unlimited Release
Printed June 2002

Enhanced Polymer Hydrogen Getters for Use in the TRUPACT-II

Hydrogen Gas Getters Evaluation Program, Phase 2 Final Report

R. Livingston, J. Duffey, T. Shepodd and P. McConnell

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/ordering.htm

SAND2002-8267
Unlimited Release
Printed June 2002

Enhanced Polymer Hydrogen Getters for Use in the TRUPACT-II

Hydrogen Gas Getters Evaluation Program,
Phase 2 Final Report

Ron Livingston, Jonathan Duffey
Savannah River Technology Center

Tim Shepodd, Paul McConnell
Sandia National Laboratories

Abstract

Addressing the needs to safely and more efficiently ship Transuranic (TRU) wastes that may generate flammable levels of hydrogen, polymer getters were previously evaluated for deployment in the TRUPACT-II. Subsequently, enhanced polymer getters, collectively known as "TRUGETTER," were formulated and pelletized, then tested against the challenging conditions defined for transport of TRU wastes. Reaction rate, reversibility, compatibility, structure/shape, passivity and capacity were evaluated. The effects of temperature extremes, radiation exposure, poisons, pressure, and free liquids were quantified.

The manufacturing parameters for production of getter powder and pellets were determined. The TRUGETTER hazards have been characterized and flammability studies completed demonstrating it is not regulated as a hazardous material by DOT. TRUGETTER is commercially available on a multikilogram scale. The precious metal content of the getters is easily recycled.

The optimum formulation of TRUGETTER pellets has a hydrogen capacity of 6.3 mol kg^{-1}. The hydrogenation rate at 5 % hydrogen, ambient temperature and 50 % getter loading is 1.2×10^{-3} mol s^{-1} kg^{-1}, and the rate is proportional to the hydrogen concentration (i.e., partial pressure). Therefore, the amount of getter required to meet the performance specification of 1.2×10^{-5} mol s^{-1} for 60 days at ambient temperature is determined by the getter capacity rather than rate. About 20 kg of getter will provide 2X the required hydrogen capacity. Reducing the temperature to –20 °F reduces the hydrogenation rate at 5 % hydrogen and 50 % getter loading to 1.4×10^{-5} mol s^{-1} kg^{-1}. The rate of hydrogen removal from air at –20 °F is about 10 times faster. Therefore, based on initial results 20 kg of getter should be sufficient to maintain the hydrogen concentration in the ICV below 0.4 % by volume even at the low temperature extreme. Codeployment of the getter with zeolite and Hopcalite® catalyst mitigates the effects of all getter poisons evaluated. The gettering reaction is not reversible under transport conditions, and increasing the total pressure from 0 psig to 50 psig has minimal impact on absorption rate. Exposure to 2.5×10^4 rad gamma radiation has minimal impact on hydrogen absorption rate and capacity.

Based on the tests conducted during Phase 2 TRUGETTER will be able to maintain a safe environment within the TRUPACT-II under the defined conditions of transport. The TRUGETTER is now ready for

Phase 3 of this project, which will involve evaluation of the engineered getter assembly in its deployed form.

Acknowledgements

The authors would like to acknowledge the following individuals for their assistance in completing various aspects of this work: Jermaine Johnson and Dean Nowak of the Savannah River Technology Center, Aiken, South Carolina; George Buffleben of Sandia National Laboratory, Livermore, California; Bradley Phillip of Vacuum Energy, Inc., Cleveland, Ohio.

Table of Contents

Page

List of Figures

Page

List of Tables

Page

Enhanced Polymer Hydrogen Getters for Use in the TRUPACT-II

Hydrogen Gas Getters Evaluation Program, Phase 2 Final Report

Introduction

Hydrogen gas getters are currently considered one of several options to support payload expansion in the Transuranic Package Transporter-II (TRUPACT-II). Current payloads are limited by a Nuclear Regulatory Commission (NRC) limit on hydrogen concentration and the established hydrogen generation rate for higher wattage waste forms. By using getters to remove the hydrogen gas generated by radioactive decomposition of waste materials, the TRUPACT-II wattage limits can be increased while maintaining the hydrogen concentrations below the 5% limit. Development of a hydrogen getter is being funded by the Transuranic and Mixed Waste Focus Area, (TMFA), through the Hydrogen Gas Getters Evaluation Program.

Under this program, hydrogen getter development is organized as a phased approach. Phase I focused on development and initial evaluation of hydrogen getter materials capable of functioning over the range of TRUPACT-II conditions. Phase 2 of the program addressed the development of an optimized formulation that meets the technical requirements (i.e., rate, capacity, temperature range, poison effects, etc.) set forth in a Statement of Work (SOW) for the Hydrogen Gas Getters Evaluation Program.[1] The follow-on to this effort in Phase 3 will address engineering issues such as the optimal size, shape, and location of getters inside of the TRUPACT-II inner containment vessel (ICV) and larger scale demonstrations under more realistic operating conditions.

Two teams of U.S. Department of Energy (DOE) scientists were funded by the TMFA to address getter enhancements needed to meet the TRUPACT-II requirements established in the SOW. This report presents the joint efforts of Savannah River Technology Center (SRTC) and the Sandia National Laboratory (SNL) to enhance the performance of commercially available polymer hydrogen getters under Phase 2 of the TMFA program. This document describes the development effort to reformulate an existing commercial product to (1) support production of getter pellets that can be mass produced using existing manufacturing facilities and (2) improve hydrogen removal rates at the extremely low temperatures required for use in the TRUPACT-II.

---

[1] U.S. DOE-TMFA, Idaho Operations Office, "Statement of Work: Hydrogen Gas Getters Evaluation Program," July 16, 1999: http://tmfa.inel.gov/Documents/SOWGetters.html.

The requirements for testing enhanced getter materials at the completion of Phase 2 are defined in a Consolidated Getters Test Plan[2] developed jointly by participants in the TMFA Hydrogen Gas Getters Evaluation Program. The results of these tests for the enhanced polymer hydrogen getters are provided as part of this report. Discussion and analysis of test results is provided to support development of the Phase 2 test plan.

Background

Polymer hydrogen getters were developed and patented[3,4,5] by SNL, and an exclusive license to produce these materials has been issued to Vacuum Energy, Inc.[6] The motivation for development of a polymer based hydrogen getter was to overcome limitations and expense associated with previously available getter materials. The commercial application of polymer getters has dramatically increased in recent years and this success was highlighted by winning a R&D 100 Award in 2001.[7] Attachment 1 contains a description of several commercial applications and the rationale for development of polymer hydrogen getters.

Phase 1 of the TMFA Hydrogen Gas Getters Evaluation Program conducted at SRTC identified the use of polymer hydrogen getters as a good candidate for the TRUPACT-II application.[8] This effort was validated by an ASME peer review[9] in December 2000 prior to initiation of Phase 2 efforts in January of 2001. At this juncture, SRTC requested the participation of SNL in the effort to enhance polymer hydrogen getter for use under the rigorous conditions defined for the TRUPACT-II. The commercial product described in the Phase I final report has subsequently

---

[2] *Consolidated Test Plan for Hydrogen Getters, Revision 3, December 20, 2001,* ***http://tmfa.inel.gov/Documents/ConsolGetters2.pdf***

[3] Shepodd, T. J.; Whinnery, L. L.; Polymer Formulations for Gettering Hydrogen. U.S. Patent 5,837,158, November 17, 1998.

[4] Shepodd, T. J.; Whinnery, L. L. Polymer System for Gettering Hydrogen. U.S. Patent 6,063,307, May 16, 2000.

[5] Shepodd, T. J.; Even, W. R.; Polymer Formulations for Gettering Hydrogen. U.S. Patent 6,110,397, August 29, 2000.

[6] Vacuum Energy, Inc., c/o Brad Phillip, 13125 Shaker Square, D-201,Cleveland, Ohio 44120, Telephone:(216) 991-7000, Fax:(216) 991-7200

[7] R&D Magazine September 2001, 43, (9), 73

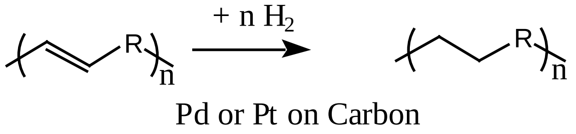
[8] WSRC-RP-2000-00901, Hydrogen Getters for Use in the TRUPACT-II, Jonathan M. Duffey and Ronald R. Livingston, Savannah River Technology Center, October 2000

[9] Assessment of Technologies Supported by the Office of Science and Technology DOE, Results for the Peer Review for FY 2001, Institute for Regulatory Science, 2001.

been tested[10] and authorized for use in onsite transportation of radioactive materials at the Savannah River Site.[11]

The SOW for the Hydrogen Gas Getters Evaluation Program defines twelve parameters that are to be evaluated as part of completing the development effort. Six of the twelve parameters defined in the SOW require laboratory tests to determine how the getters' hydrogen capacities and reaction rates are affected by transportation conditions[12] of the TRUPACT-II. The test results for each parameter are described in the following sections under the applicable Hydrogen Gas Getters Evaluation Program parameter. Attachment 2 contains a copy of the test matrix defined in the consolidated test plan.

The underlying basis of hydrogen getter operation is a chemical reaction that uses hydrogen gas to reduce carbon-carbon double or triple bonds. This hydrogenation reaction is used to manufacture commercial products like margarine and cyclohexane. Hydrogenation of saturated compounds requires a precious metal like platinum or palladium to catalyze the reaction at modest temperatures and pressures. This reaction proceeds as follows:



In the presence of both hydrogen and oxygen, a precious metal will preferentially catalyze the formation of water in a reaction known as recombination. Under conditions where water can be tolerated, this is often a desired effect because the reaction removes both hydrogen and oxygen, thus more quickly reducing the potential for hydrogen related accidents. Recombination does not consume the capacity of the getter. Once oxygen is depleted, the hydrogenation reaction will continue to remove hydrogen until the getter capacity is exhausted. Under conditions anticipated for the TRUPACT-II, both catalytic reactions are expected since the container is sealed in air, which contains approximately 21 % oxygen. The relative rates of hydrogenation and recombination vary with the concentration of the reactants, but at low hydrogen concentrations (e.g., <1 %) recombination is observed almost exclusively until the oxygen concentration is below a few percent.

---

[10] WSRC-TR-2001-00105, Test Results for Implementation of Hydrogen Getter in the DDF-1 Shipping Package, Ronald R. Livingston and Jonathan M. Duffey, Savannah River Technology Center, March 2001

[11] WSRC-SA-99-00006, Onsite Safety Assessment for Transport of Mixed Oxide Scrap in the DDF-1 Packaging, Rev. 2, Westinghouse Savannah River Company, April 2001.

[12] The "normal conditions of transport" are defined in 10 CFR Part 71, "Packaging and Transportation of Radioactive Material."

The hydrogen removal rates and capacities of each hydrogen getter are measured under the conditions established by the consolidated test plan. The objective in the consolidated test plan is to provide a consistent means by which to evaluate and compare hydrogen getters proposed for use in the TRUPACT-II. The test plan incorporates a range of test conditions deemed to approximate TRUPACT-II environments and which may anticipate regulatory questions regarding getter performance in the TRUPACT-II. The getter performance data resulting from these tests will be used to support ongoing evaluation, system design, and regulatory approval of a getter assembly for the TRUPACT-II. Hydrogen removal rate and capacity determine the quantity of getter needed to meet the hydrogen removal rate of 1.2×10^{-5} moles per second (mol s^{-1}) specified by the SOW.[13] Other test conditions are specified to evaluate the impact of transportation conditions on getter performance including temperature, poison vapors or gases, gas composition (e.g., air or nitrogen), etc. Because the test apparatus design(s) and other factors have a significant impact on gas transport and influence the desired measurements, the consolidated test plan proposed evaluating the getter response to test conditions by comparing the test cases with an experimental control.

As a basis of comparison between getter materials, the rates of hydrogen absorption (i.e., hydrogenation) at low getter loading and approximately 50 % capacity were measured over a range of hydrogen pressures equivalent to 5 % and 1 % H_2 in N_2 at ambient temperature (approximately +77 ^{o}F) and pressure. These measurements support the assessment of how rates of hydrogen removal are affected by hydrogen concentration. Once the relationship between hydrogen absorption rate and hydrogen concentration was established, subsequent tests focused on measurement of hydrogen removal rate at a hydrogen pressure equivalent to 5 % hydrogen at 1 atm total pressure (i.e., 38 Torr). Tests were also conducted using the getter materials being developed by the second team of scientists working at INEEL and LANL. These results are presented to support comparison of test results between the two candidate getter materials and test approaches.

Polymer Getter Enhancement

At the conclusion of Phase I, SRTC identified two enhancements needed to improve the commercially available VIP polymer getter for use in the TRUPACT-II: (1) production of getter in pellet form and (2) increased rate at low temperature. During the first nine months of 2001, SNL focused on producing enhanced formulations of polymer getter based on existing commercial products. These new formulations are collectively called “TRUGETTER”. As

---

[13] Personal communication from Murthy Devrakonda of Westinghouse TRU Solutions, Carlsbad, NM, May 23, 2002. This hydrogen generation rate from the SOW is based on 14 drums containing 7.6 watts each with no bags and a 5X filter in the drum. This configuration exceeds the 40-Watt limit, therefore the specified rate is conservative by a factor of more than two.

laboratory-scale formulations were produced in the SNL facilities, baseline performance was measured to evaluate the effects of different enhancements on reactivity and capacity. Attachment 3 describes the acceptance testing completed by SNL to measure baseline performance of all new polymer getter materials. SRTC subsequently performs a series of experiments that evaluate the getter performance specifics for TRUPACT-II on a limited subset of the laboratory-scale formulations.

Sufficient progress has been made in the current formulation of TRUGETTER to overcome problems associated with producing quality pellets. Both getter powders and pellets described in this report were produced using industrial equipment and procedures capable of high-volume mass production. A second advancement in the formulation of TRUGETTER has provided a factor of 20 increase in hydrogenation rate of polymer getter powders at ambient temperature. This improvement supports the desired reaction rate needed at low temperature and helps offset the anticipated loss in rate with forming pellets. Additional improvements in getter formulation that may be identified in subsequent testing or preparation for getter deployment (e.g. Phase 3 testing) should require only small, incremental changes in getter formulation. For example, additional minor changes may be helpful to optimize the precious metal catalyst content of TRUGETTER.

TRUGETTER is manufactured using techniques developed under the SNL license with Vacuum Energy. Many details of getter production remain proprietary even though the U.S. Government retains an unrestricted license of all hydrogen getter technologies patented by SNL. However, no proprietary information concerns preclude the successful development of polymer hydrogen getters for the TRUPACT-II or other shipping containers. Attachments 4 and 5 include Material Safety Data Sheets (MSDS) for each TRUGETTER product (both powder and pellets) developed under Phase 2 of the TMFA’s Hydrogen Gas Getter Evaluation Program.

The laboratory-scale production of TRUGETTER progressed to pilot-scale manufacture using industrial equipment identical to that used to efficiently produce thousands of kilograms of commercial getters. The SNL licensee of polymer getter technology conducts these pilot tests under technical direction from SNL and SRTC personnel. Usually, “dummy getter” batches (getter without the precious metal catalysts) are used to explore processing parameters. Precious metal catalysts are used once the manufacturing process is finalized. Including precious metals in the final formulation has little influence on the processing parameters, as it is a small portion of the total formulation, although a significant fraction of the cost of the getter.

The industrial-scale process for getter manufacture differs from the laboratory-scale process. SNL has optimized the process for large-scale production through experience with commercial forms of the polymer getter. The polymer getters are made from polymer, catalyst, and additives for chemical reactivity and mechanical strength. The hydrogenation reaction is a heterogeneous gas-solid reaction dependent on the composition and surface area of the getter. Simple mixing of the components yields reactivity towards hydrogen, but process optimization is necessary to yield a fully functional getter. Proper processing yields up to a million times greater reactivity from the same ingredients as well as greater chemical and physical stability.

Specifically, during processing there is a balance between the forces needed to mix the ingredients and the requirement not to overwork the mix and suffer reduced reactivity. The reaction rate is a function of how uniformly the catalyst can be dispersed among the polymer reactive sites (the double bonds that eventually react with the hydrogen). The polymers are melted and dispersed into the dry ingredients. Insufficient mixing yields lower reactivity as the polymer must diffuse to the reactive catalyst sites. Too much mixing yields a low surface area material that relies on extensive hydrogen diffusion and thus has slower reactivity. Insufficient heating makes it difficult to disperse the polymer. Excess heating will lower the surface area of the getter and reduce its reactivity.

Ingredients

The following section discusses the rationale for the selection of the individual ingredients that make up the hydrogen getters. Specific proportions, ingredients, and formulation procedures are proprietary information of Sandia National Laboratories and its licensee Vacuum Energy, Inc. and are not disclosed in this report. An MSDS is provided for the general formulation of polymer getters in Attachment 4.

Catalyst

Precious metal catalysts make the getter work. Without them hydrogen is not reactive towards carbon-carbon multiple bonds at interest for this application. The catalyst is usually palladium on carbon though platinum on carbon is useful in certain poison situations.[14] Reactivity is proportional to metal concentration in the getter. Higher amounts of lower concentration catalysts are more effective. For example 10 wt.% of 1 % Pd/C will give a more reactive getter than 1 wt.% of 10 % Pd/C even though the net metal content is the same.

Hydrogen Receptors

The carbon-carbon multiple bond content of the material represents the capacity of the getter. The backbone of the polymer getters is polybutadiene and its copolymers. Butadiene polymers are the backbone of many elastomeric materials or rubbers. Butadiene can be polymerized in a 1-4 fashion yielding a linear polymer containing *cis* and/or *trans* double bonds. Butadiene can

---

[14] Buffleben, G. M.; Shepodd, T. J. *The Effects of Temperature and Carbon Tetrachloride on Polymer Based Precious Metal Hydrogen Getters*; SAND2000-8262; Sandia National Laboratories: Livermore, CA, December 2000.

also be polymerized in a 1-2 fashion yielding a linear saturated chain appended with vinyl groups. In practice, most butadiene polymerizations are a mixture of 1-4 and 1-2 depending on reaction conditions and the nature of the polymerization catalyst. Increasing the 1-2 polymerized fraction for polybutadiene of a given molecular weight will substantially increase the viscosity (or lower the melt flow index) making processing more difficult. Polybutadienes are available as free-flowing liquids with molecular weights in the thousands and as solids having molecular weights in the millions. Polybutadienes are cross-linked (cured) with free radical initiators (peroxides) and/or vulcanized (sulfur), then molded into stable macromolecular structures such as tires and radiator hoses. Cross-linking is generally undesirable in hydrogen getters.

Butadiene is copolymerized with other monomers because it brings an elastomeric quality into otherwise brittle polymers. Copolymers with styrene are used as tough, yet flexible, polymers in items such as hoses and shoe soles. Copolymers with polystyrene and acrylonitrile yield strong yet impact resistant plastics (ABS) for toys and consumer products.

Getters use uncured polybutadiene and its copolymers (we may just say “rubber” in this report) as a source of double bonds that will be reduced by hydrogen in the presence of precious metal catalyst. The material properties of the polymers are only important as they support the engineered form of the getter.

Other Ingredients

Bulk Media for Physical Properties

As much as two thirds of the mass of a polymer getter can be inert material, usually carbon black. The carbon properly disperses the rubber into a form where it can migrate to the catalyst, which is also carbon black based. Carbon blacks come in many forms.

Co-getters and Flammability Modifiers

Getters may also be formulated with scavengers for other species. Co-getters are deployed as part of the getter pellet or deployed adjacently in the engineered assembly. The molecular sieves that we deploy to scavenge the water from recombination are an example of such a co-deployed getter.

Small amounts of non-combustible materials are added to getters with high precious metal content as needed to temper their flammability. Flammability determinations as described in Attachment 6 determine the need for such additives, if any.

Preservatives

Two kinds of preservatives are used in the polymer hydrogen getters. First, a phenolic antioxidant is added to minimize ongoing oxidation by atmospheric oxygen. Second a carbon radical scavenger is added to shut down any radical-initiated cross-linking that may be caused by excess heat or radiation.

Pelletizing Aides

Because polymer getter is produced as a fine black powder, pelletization is an important step to improve handling in the TRUPACT-II application. Pelletization does little for getter performance, although pellets facilitate gas transport to the middle of a large bed of material. The gas path remains coherent throughout the bed of pellets. Powders can compact under their own weight yielding inhomogeneous samples with performance that does not match that of laboratory experiments. Importantly, pellets are easier to physically manipulate and facilitate deployment engineering.

The getter is first manufactured as a fine black powder. Though non-hazardous, it is difficult to handle and transport. Most commercial getter/recombiner products are supplied as pellets simply because they are easier to handle and yield consistent performance. Unfortunately, every commercial getter has a different pelletization process. Pelletization also simplifies the cleanup of spills.

Pelletization is a straightforward process of compaction either by pressing powder into a mold or by extrusion through a die. Often additives such as binding agents are blended with the free flowing powders to produce a pellet with sufficient final strength. Volatile solvents used to disperse the binding agents may need to be evaporated after the pellets are formed.

Pellets are characterized by their crush strength. Pellets having a crush strength of >1 kg are recommended for this application. (A pellet with a 1-kg crush strength can be broken by pressing a thumbnail firmly into its side.) The mechanical properties of the getter pellets need only to be sufficient to support the weight of the pellets above them and to survive the vibration of over-the-road transportation. Getter pellets of high strength can be produced, but this requires either copious additives, that reduce the effective capacity, or extreme compaction that reduces the hydrogen removal rate of the getter.

The TRUGETTER has a requirement for higher rates at low temperature as compared to most commercial getters so the pelletization processes used for other getters are not suitable. In FY01, SNL interacted with the catalyst manufacturer Engelhard Corporation to pelletize the getter. Engelhard manufactures large quantities of different catalyst pellets and they understand the need not to poison the precious metals. Engelhard manufactured a number of pellet types using different binders, drying conditions and extrusions. They optimized production conditions using dummy getters and finally produced functional getters containing precious metals.

Through this effort, the effects of different binding agents and drying conditions on getter performance (reactivity) were evaluated. Eventually, Engelhard was able to select binding agents that did not adversely affect getter reactivity. As expected, getter pellets show a slightly reduced reactivity towards hydrogen via both gettering and recombination mechanisms as compared to the powdered getters from. This is observed in all pellet manufacture as the surface area is reduced slightly during compaction. There is also a reduction in capacity proportional to the amount of inert binding agent added. For the Englehard pellets tested under the Consolidated Test Plan, the rate and capacity were reduced by 50 % and 10 %, respectively, as compared to the getter powder.

Material Compatibility/Transportation Concerns

Polymer hydrogen getters are non-hazardous materials that show no reactivity with the materials contained within the TRUPACT-II shipments (except for the gases). They have similar bulk reactivity to a ground up automobile tire. They are combustible but difficult to ignite and are self extinguishing in many situations. As with many organic materials, contact with strong oxidizing agents should be avoided.

All hydrogen getters have one materials compatibility concern that must be addressed. Because of the reactivity of the finely divided metals, the catalysts used to manufacture the getters are DOT classified flammable solids when dry. As such, getters and other materials formulated from flammable solids must be demonstrated to not have the hazardous characteristics of their ingredients before they can be shipped legally as non-hazardous. All SNL developed polymer getters have been rigorously tested and found to be non-flammable solids. Examples of the testing procedure are found in Attachment 6. All of the polymer getters (powders & pellets) may be shipped as non-hazardous materials (new or hydrogenated) and are not regulated by DOT.[15]

The heat of reaction during the most rapid hydrogenation or recombination is insufficient to ignite or even char a pellet bed of hydrogen getter. If for any reason the polymer getters do get extremely hot, they will start to cross-link, losing their reactivity but not releasing scavenged hydrogen. Polymer getters do not have a specific upper temperature limit, however hydrogen getters start to gradually and irreversibly lose their reactivity through cross-linking at temperatures exceeding 160 to 200 °C.

---

[15] United Nations, Transport of Dangerous Goods, Manual of Tests and Criteria.

Polymer Getter Testing & Evaluation – Required Measurements

Rate and capacity measurements are used to characterize getter performance and to determine how getter operation is affected by normal conditions of transport identified for the TRUPACT-II. The hydrogen removal rate measurements for both hydrogenation and recombination mechanisms are made as a function of hydrogen concentration and temperature. Other parameters identified in the consolidated test plan, like potential poisons, radiation, and reversibility, are evaluated by comparison of test results for samples exposed to the test condition(s) with an experimental control. Controls used in this evaluation are set-up to match the test sample as closely as practical (e.g., getter mass, gas volume, gas composition, gas pressure, temperature, etc.) to simplify evaluation of getter performance.

Rate

Rate measurements were conducted in air and inert atmospheres (e.g., nitrogen or argon) to evaluate both the recombination and hydrogenation reaction rates, respectively. The rate of hydrogen removal decreases as getter capacity is consumed and as hydrogen concentration and temperature decrease. Consequently, performance of the getter is presented at both low hydrogen loading and at 50 % of the measured capacity to support further evaluation. The hydrogen absorption rates are expressed in units of moles of hydrogen per second per kilogram of getter (mol s^{-1} kg^{-1}).

In some cases, the hydrogenation rate was measured in vacuum to avoid gas transport-limited hydrogen removal observed in the small-scale test apparatus. This occurs when the small vessel dimensions limit mixing by natural convection, thus complicating measurement of hydrogen removal rates.[16] Alternatively, the rate of hydrogen removal from air or nitrogen was measured in a small-scale vessel modified to intentionally limit diffusion of hydrogen through the tubing attached to the sample container to the manifold. This vessel was used to measure rates in air and nitrogen at ambient and elevated temperature to help better understand the dynamics of gas transport. Because the rate of hydrogen diffusion through the tubing was much slower than the rate of hydrogen removal from the more open sample container, we observed two distinct rates of pressure drop. The first was a relatively rapid pressure drop corresponding to hydrogen removal from the vessel interior. The second was a much slower pressure drop associated with diffusion of hydrogen from the tubing into the vessel interior from which it was rapidly removed by reaction with the getter. At lower temperatures the small-scale vessels were used unmodified

---

[16] Tests in the larger 5L test apparatus, where convection was not limited by vessel dimensions, have shown that hydrogen absorption rates in vacuum and inert atmospheres are essentially identical.

because diffusion through the apparatus was fast relative to the reaction rate at the lower temperatures.

The data in Table 1 are provided to demonstrate the similarity in hydrogenation rates measured in vacuum for both types of small-scale vessels and for different fill gases with the modified vessel. The rates in vacuum for the two different vessels are in good agreement with a relative standard deviation of ± 5.2 %. The rates measured in nitrogen and in helium in the diffusion-limited vessel are essentially identical. The average of the rates in vacuum is about 32 % higher than the average of the rates in nitrogen and helium.

Table 1. Hydrogenation rates for 20TS151C pellets at low loading and 22 °C.

Apparatus	Rate (mol s-1 kg-1)		
	Vacuum	Nitrogen (~ 600 Torr)	Helium (~ 600 Torr)
Regular	2.12E-03	N/A	N/A
Diffusion-limited	1.97E-03	1.56E-03	1.54E-03

Capacity

The getter capacity is defined as the quantity of hydrogen removed by a getter material when operated in an inert atmosphere.[17] The capacity of each getter material may be effectively measured in either vacuum or an inert gas like nitrogen or argon, and the capacities of the getters will be expressed in moles of hydrogen per kilogram of getter (mol kg^{-1}). The capacity of each getter material is measured with an excess of hydrogen remaining after hydrogen removal has decreased to a very slow rate (e.g., less than 1.2×10^{-6} mol s^{-1} kg^{-1}). The temperature is allowed to increase during hydrogenation to accelerate the hydrogen removal reaction. In actual operation within the TRUPACT-II, the getter is likely to be installed in an air atmosphere and will generate water vapor rather than consume hydrogen capacity until the oxygen is consumed. However, no credit is taken for the recombination reaction as part of determining getter capacity because the presence of adequate concentrations of oxygen inside the ICV cannot be assured because oxygen may also be removed by radiolysis.

---

[17] In the presence of oxygen, the noble metal hydrogenation catalyst will also catalyze the recombination of hydrogen and oxygen to form water, thus complicating an accurate determination of getter hydrogenation capacity.

Rate Calculations

The test apparatus used at SRTC is designed to facilitate the measurement of pressure, volume, and temperature (PVT) in a static system (no flowing gas). The PVT data are then used to calculate hydrogen absorption rates and capacities for the various getter materials and test conditions. The hydrogen absorption rate for a given sample size and degree of hydrogen loading was determined by plotting the natural logarithm of the hydrogen pressure proportional to the molar hydrogen concentration versus time (Figure 1). At constant temperature this plot yields a straight line, the slope of which provides a pseudo first-order rate constant that is independent of hydrogen concentration and can be used to calculate hydrogen absorption rate at a specific hydrogen concentration.[18] This reaction rate analysis holds for small additions of hydrogen that consume only a small fraction of the total getter capacity (i.e., when the concentration of double bonds is in large excess relative to the concentration of hydrogen).

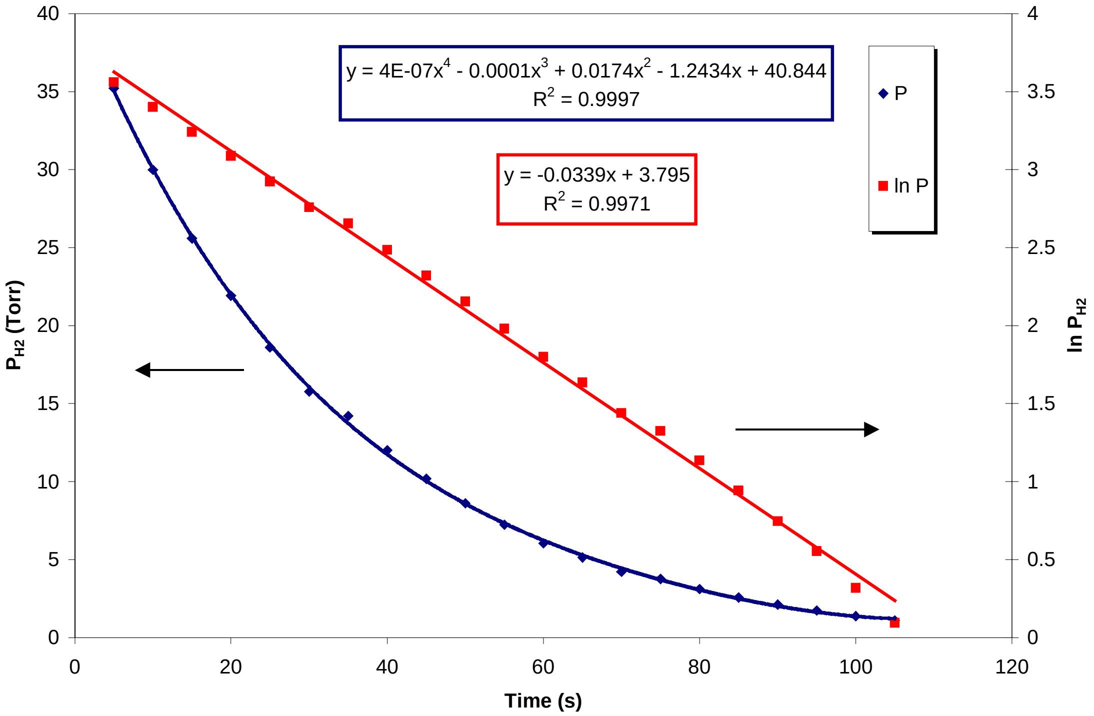


Figure 1. Calculation of hydrogen absorption rate from pressure vs. time data for 20TS151C pellets at 71 °C.

The rate of pressure drop measured in these tests depends not only on temperature and hydrogen concentration but also on the sample size and container volume. Therefore, the pseudo first-order rate constant k (s^{-1}) can be multiplied by the container volume (L) and divided by the

---

[18] Atkins, P. W., Physical chemistry, 4th Edition, W. H. Freeman and Company, New York, 1990, pp. 780-787

sample mass (kg) in order to express the rate constant (k′) in terms useful for other applications (i.e., L s^{-1} kg^{-1}). This rate constant can subsequently be used to calculate rate by multiplying by the molar hydrogen concentration for the desire hydrogen pressure (e.g., 5 % hydrogen at ambient temperature and one atmosphere pressure is 0.0021 M). Therefore, by definition the rate of hydrogen removal is 5 times faster at 5 % (or 38 Torr) hydrogen than at 1 % (or 7.6 Torr) hydrogen as long as the pseudofirst-order kinetics apply. Likewise, the rate will double if the mass of getter is doubled. Prior experience demonstrated that this type of rate analysis could be effectively applied to scale-up for getter assembly design.

Alternatively, the pressure versus time data can be curve fit and a first derivative of the equation for this curve used to determine the instantaneous rate at a specific hydrogen pressure based on the elapsed time at this pressure. This type of first derivative analysis provides results that are very similar to those obtained from the pseudo first-order analysis (Table 2).

Table 2. Rate of hydrogen removal by 20TS151C pellets at 71 °C as a function of hydrogen pressure.

Hydrogen Pressure (Torr)	Volume Fraction of Hydrogen at 1 atm Total Pressure (%)	Rate (mol s^{-1} kg^{-1}) Pseudo first-order Analysis	Rate (mol s^{-1} kg^{-1}) First Derivative Analysis
38	5	3.90E-03	3.52E-03
7.6	1	7.79E-04	7.29E-04

Equipment Design

Small-scale apparatus

Testing at SRTC utilizes two vessel geometries: a small-scale system consisting of vessels approximately 60 mL in total volume and a large-scale apparatus approximately 5 L in total volume. Figure 2 is a schematic showing how the small vessels and gas manifold used in these experiments are configured. This schematic shows only one of the vessels attached to the manifold. This arrangement simplifies the addition of an accurately known amount of gas to the sample. The gas manifold was constructed of stainless steel sample containers and calibrated volumes, stainless steel tubing, Cajon® fittings, and Nupro® valves. The sample beds were designed to accept a 4-dram glass sample vial in an upright orientation to facilitate sample introduction and removal. Bed temperatures were monitored by thermocouples (type J) inserted into holes drilled into the walls of the beds and extending from the bottom to a point approximately halfway to the top of the beds. The volumes of tubing between valves were calibrated so that known gas volumes could be introduced to the sample chamber.

The gas pressures are measured by MKS Baratron® pressure transducers (10,000 Torr range; 0.1 Torr readability). A Varian milliTorr vacuum gauge was also used to measure the manifold pressure when open to vacuum. Electrical resistance heaters fitted to the sample beds and connected to Cole Parmer Digisense temperature controllers were used to heat the sample beds for the experiments at elevated temperature. A Neslab® refrigerated circulating bath was used to cool the sample beds for the low temperature experiments. Date, time, temperature, and pressure data were recorded and monitored via LabView® computer software. The first three photographs in Attachment 7 show this arrangement.

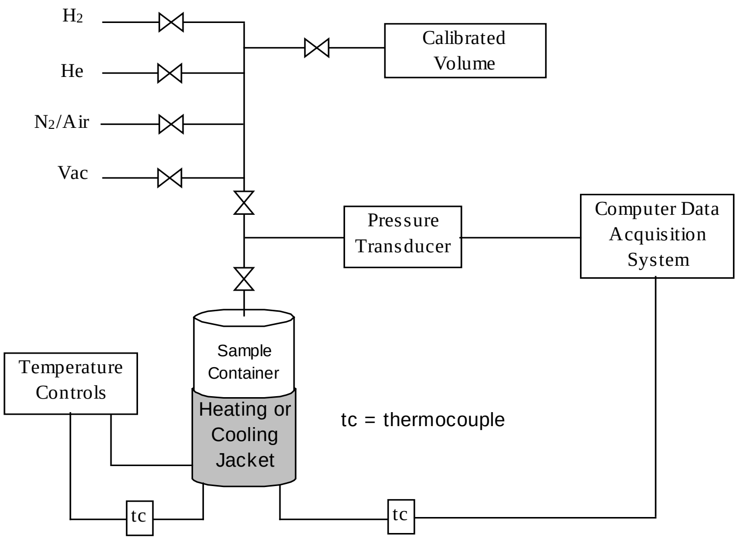


Figure 2. Schematic of hydrogen getter test apparatus.

Measurements are initiated by placing the getter material in a fixed volume container and adding hydrogen gas or gas mixture to provide the desired hydrogen concentration at a known pressure and temperature. The resulting pressure drop with time is recorded and used to calculate the getter's hydrogen removal rate as described previously. Figure 3 illustrates this process.

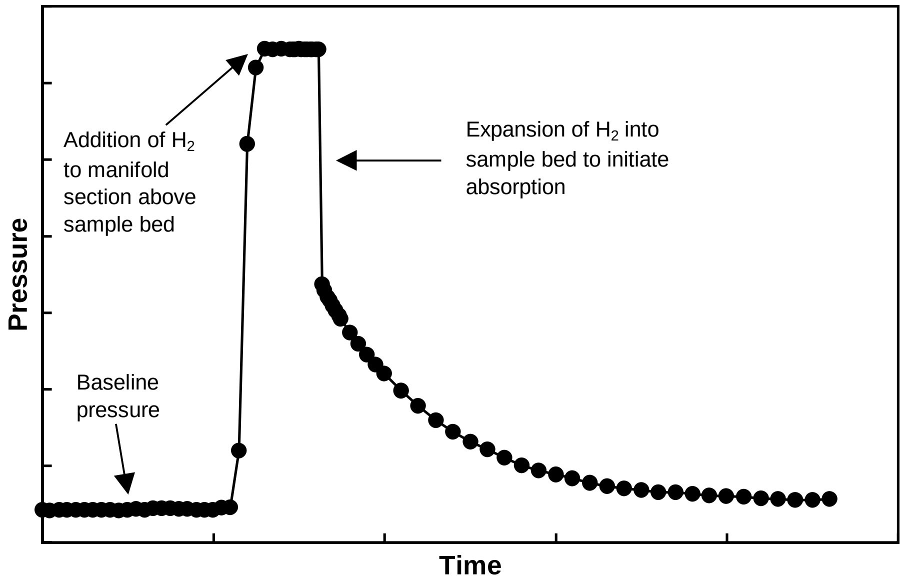


Figure 3. Hydrogen absorption curve for a polymer hydrogen getter.

Large-scale apparatus

Some of the tests presented in this report were measured in a second, larger test vessel constructed using a 5.1-L stainless steel, double o-ring seal container (the primary containment vessel or PCV from the DDF-1 shipping package). The PCV was modified with stainless steel tubing and fittings to allow for gas introduction, evacuation, and sampling. A schematic of this apparatus is shown in Figure 4 below and photographs are provided in Attachment 7. In some tests, a borosilicate glass insert was used to reduce the container free volume to approximately 2.5 L.

All connections to the PCV are made at the vessel bottom to minimize changes to the vessel geometry. Prior to use for hydrogen getter testing, the test apparatus was leak tested to assure any leaks were sufficiently small to have no impact on measurement accuracy. The pressure sensors are MKS Baratron® Series 690 sensors (0 to 5000 Torr or 0 to 10,000 Torr). The apparatus is equipped with a Series 203 Variable Leak Valve (Granville-Phillips) to allow addition of hydrogen from a 1-L standard volume to the PCV at the desired rate to simulate hydrogen generation from within the container. This standard volume is used to supply hydrogen to the variable leak or make addition of gas mixes directly to the PCV. Two thermocouple sensors are positioned inside the PCV to monitor the temperature of the gas phase and getter materials. An additional thermocouple is positioned outside the PCV to monitor the temperature of the air in the laboratory.

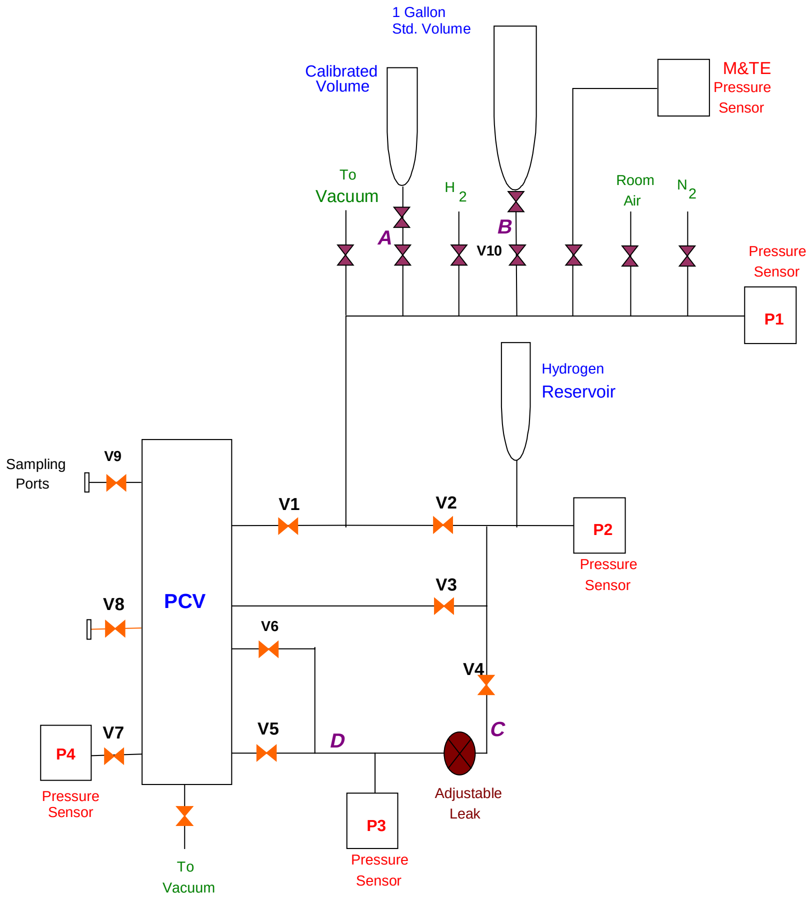


Figure 4. Schematic of large test apparatus.

The gases used in these tests include hydrogen, helium, nitrogen and air. The hydrogen is supplied from a size b cylinder located within the lab module where these tests were conducted. This hydrogen is supplied at a minimum purity of 99.95 %. The nitrogen and helium gases used in these tests are from the house gas system and is supplied from cryogenic tanks of the respective liquid. The air used in these tests is either room air that has been filtered to remove any particles or air from the house gas system.

Equipment Calibration

Thermocouples

Calibration checks for thermocouples used in these tests were previously conducted by comparing the response of the thermocouples with a NIST traceable, calibrated temperature device. The calibration range spans –30 °C to +100 °C. The measurement accuracy was better than ± 1 %.

Pressure transducers

Pressure calibration checks of the pressure transducers were completed using a NIST traceable, calibrated Paroscientific pressure transducer installed on the apparatus manifold. The system was evacuated, then nitrogen gas was metered into the manifold to raise pressure in various increments over the range of interest. Response of the Baratron sensors was typically within 0.6% of the calibrated transducer. Typical accuracy is ± 0.08 %.

Vessel volumes

The various volumes of the large-scale test apparatus were determined using a one-gallon standard volume. Volumes of the test apparatus relative to the standard volume were determined at ambient temperature (~ 22 ºC) by one of two processes. In all cases, pressures were read from a single pressure transducer. Temperature remained essentially constant during the calibration process. In the first process, nitrogen was introduced into the one-gallon standard volume V_1 at an initial pressure P_1, then expanded into the previously evacuated tubing V_2 and unknown volume V_3 to obtain a new pressure P_2. The apparatus was evacuated, then nitrogen was introduced into V_3 at a second initial pressure P_3 and expanded into V_2 and V_1 to obtain P_4. This process minimizes the propagated uncertainty in the unknown volume calculation because the volume of the connecting tubing V_2 can be algebraically canceled. V_3 is given by the following equation:

$$V_3 = P_1 \text{ x } P_4 \text{ x } V_1/(P_3 \text{ x } P_4).$$

The volumes of the one-liter vessel and the empty PCV were determined in this manner. Similarly, the manifold and hydrogen reservoir volumes were determined in this manner using the newly calibrated one-liter volume as V_1.

The remaining volumes of the apparatus were determined by expanding nitrogen at a known pressure P_1 from a known volume V_1 into the unknown volume V_2 to obtain the final pressure P_2. V_2 was then calculated from Boyle's Law:

$$V_2 = P_1 \text{ x } V_1/P_2.$$

The uncertainties in the volume measurements are typically less than one percent. A similar procedure was employed for the small-scale test apparatus using a 150-mL standard volume.

Sample mass

Samples were weighed using a Mettler model PM6100 balance, which is readable to 0.01 g, or an Ohaus model GA200, which is readable to 0.0001 g. Standard weights were used to confirm balance performance periodically during use and both balances have NIST traceable calibrations.

These checks showed that mass measurements were consistently within control limits established for these balances.

Leak Checks

All apparatus components have been leak checked by evacuating the components and measuring pressure rise with time (rate of rise). Leak rate Q (std. $cm^3\ s^{-1}$) is calculated using the following equation.[i]

$$Q = \frac{(P_{final} - P_{initial}) \times V \times 1.32}{(t_{final} - t_{initial})}$$

In this equation, P is pressure measured in Torr and corrected to standard temperature, V is the test volume in liters, and t is time in seconds. The factor 1.32 is used to convert from Torr•liter (at standard temperature) to std. cm^3. The leak rates measured for this apparatus are generally less than $1x10^{-6}$ std. $cm^3\ s^{-1}$ (5×10^{-11} mol s^{-1}), which is more than adequate for the current testing.

Sample Preparation

Samples were used as received or conditioned as specified in the consolidated test plan according to the requirements of a particular test. Pretreatment included irradiation with cobalt-60 gamma rays, extended storage at elevated temperature, moisture adsorption at 100 % relative humidity, etc.

Small-scale tests

In the small-scale apparatus, samples were typically measured in glass sample vials (e.g. 1, 2, or 4 dram depending on sample size) if the test was run in vacuum. For tests run at higher pressures, the samples were generally placed directly into the stainless steel test vessel. This is expected to minimize the variation between measured hydrogen removal rates associated with a diffusion-limited geometry in glass vials of various sizes. In each case the sample was weighed to the nearest 0.1 milligram.

Large-scale tests

Samples run in the PCV were placed into a wire basket developed to hold both the getter sample and zeolite in a dimensional geometry scaled to the size of a 55-gallon drum. The mass of getter and zeolite were recorded to the nearest 0.01 g for these tests.

Attachment 7 contains photographs of the sample container, getter pellets, and zeolite used for the tests conducted in the PCV. The getter pellets were reduced in size (~ 1/8” diameter by 1/8” long) to fit into the inner basket and 13X zeolite was used to fill the annular space surrounding the getter. Based on calculation of the potential water generated and free liquid in the

TRUPACT-II a zeolite: getter mass ratio of 4:1 of was selected for these tests. This required the wire basket shown in Attachment 7 to hold 0.5 g of getter pellets and 2.0 g of zeolite. The dimensions of this wire basket are approximately 0.63 inches outside diameter and 1.0 inches tall. The inner basket has an outside diameter of 0.31 inches and is 1.0 inch tall. When scaled to the size of a 55-gallon drum, these inner and outer baskets will hold approximately 50 L and 225 L respectively.

Experimental Results

Test results are compiled and presented in the same order as listed in the consolidated test plan although tests were not necessarily conducted in this sequence. The specifics of each test are described and representative sample results (i.e. pressure, temperature, time) plotted to support discussion of the test data. Results of each test are tabulated following calculation of the desired parameter. Calculations have been completed using a Microsoft Excel spreadsheet. The results of these tests will be used to (1) provide the baseline material characterization needed to address design of a getter assembly for use in the TRUPACT-II and (2) to begin dialog with the NRC on use of hydrogen getters for shipping radioactive materials. Future efforts (Phase 3) will address the impact of packaging the getter in a form required for deployment.

Getter Operational Life (capacity)

Theory

The scavenging capacity of an unsaturated organic hydrogen getter is theoretically one mole of hydrogen per mole of double bonds or two moles of hydrogen per mole of triple bonds. Practically, hydrogen getters reach only 70 to 95 % of their theoretical capacity under ambient reaction conditions. As the hydrogenation reaction proceeds, the un-reacted carbon-carbon multiple bonds become further diluted by hydrogenated species and the rate of hydrogen scavenging is decreased. Typical polymer getters have theoretical capacities ranging from four to nine mol kg^{-1} and are expected to have a working capacity 10 to 25 % less than theoretical.

Test description

Capacity measurements were conducted by placing a weighed sample of the selected getter material into a small vessel as described previously. The sample mass for polymer getter powder and pellets was typically 0.10 g. The sample was evacuated for 30 to 60 minutes or longer at ambient temperature to remove most of the atmospheric oxygen present in the sealed container. Typically the pressure remaining in these vessels was less than 3×10^{-2} Torr.[19] The sample vessel was then sealed and exposed to a known volume and pressure of hydrogen at ambient temperature. The volume of hydrogen was nominally 60 cm^3 and pressures range from 450 to

485 Torr. The pressure drop resulting from hydrogenation of the polymer getter was measured over a period of time ranging from one to several days with a hydrogen over pressure of approximately 200 Torr remaining at the conclusion of each test. The hydrogen removal rate at this point had usually decreased to less than 1 x 10^{-6} mol s^{-1} kg^{-1}.

Test results

Figure 5 shows the amount of hydrogen removed over time by the TRUGETTER powder and pellets selected for evaluation opposite the consolidated test plan criteria. Note that the capacity of the getter pellets is reduced by approximately 10 % compared to the powder as a result of binders added during pellet manufacture. The increased time required for the pellets to remove a given amount of hydrogen is an indication of a decreased rate of hydrogen removal relative to the powder. Differences in rate between materials may be exaggerated by this test because the large amount of hydrogen added causes the faster getter materials to reach a higher temperature. Consequently rate measurements are made with much smaller additions of hydrogen to avoid large changes in both the sample temperature and degree of hydrogenation.

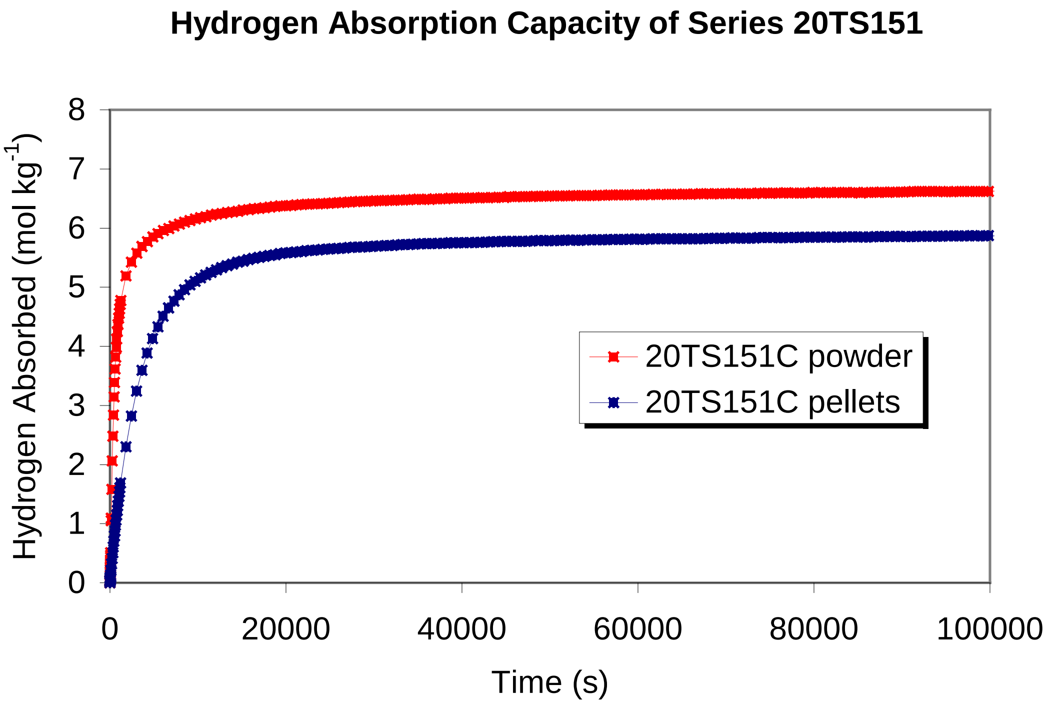


Figure 5. Hydrogen absorption capacity of TRUGETTER.

---

[19] The quantity of oxygen present in the test vessel at this pressure would result in an error of less than 0.0005 mol kg^{-1} in the measurement of getter capacity.

Table 1 shows the capacity measurements and initial rate for multiple TRUGETTER samples considered for full characterization against the consolidated test plan criteria. Capacity measurements from SRS and SNL were in good agreement and ranged from 65 % to 97 % of theoretical. Sample 20TS151B powder had the highest theoretical and measured capacities, but the capacity of the pellets decreased by 35 %. In contrast, the capacity of 20TS151C powder decreased by only 10 % upon pellet formation, as was expected based on the amount of additives used to facilitate pelletization.

Table 3. Capacity Data for Polymer Getter Formulations.

Sample Identification	Theoretical Capacity (mol kg^{-1})	Capacity (SRS) (mol kg^{-1})	Capacity (SNL) (mol kg^{-1})	Initial Rate (SNL) (mol s^{-1} kg^{-1})
20TS151A powder	7.94	7.37	7.41	1.65 x10^{-4}
20TS151B powder	9.77	8.98	9.02	4.91 x10^{-4}
20TS151B pellets	8.79	5.77	5.80	0.85 x10^{-4}
20TS151C powder	6.92	6.72	6.53	9.82 x10^{-4}
20TS151C pellets	6.23	5.84*	5.89	4.91 x10^{-4}
20TS151D powder	8.21	7.35	7.21	7.59 x10^{-4}

Initial rate measurements performed at SNL for acceptance testing
*Average of 3 replicates with a standard deviation of 0.10 (1.7 %)

Sample A is similar to VIP getters used in previous testing. Samples B and C are two different TRUGETTER formulations produced using the commercial-scale process. These same formulations were previously produced using the bench-scale process at SNL and screened for use in the TRUPACT-II. Sample D is similar in composition to Sample C but contains a higher percentage of polymers not attainable in the bench-scale process. Pellets were produced for Samples B, C and D, but the quality of D pellets was considered inadequate for use in the TRUPACT-II application.

Selection of Getter Pellets

Samples 20TS151B and 20TS151C powders have improved rates and capacities relative to the VIP getter used in previous tests.[20] Pellets produced from 20TS151C powder have superior performance under these conditions and were selected for complete characterization following the consolidated test plan. Sample C powder was also characterized under portions of the consolidated test plan to demonstrate the impact that pelletization has on polymer hydrogen getter performance.

---

[20] Duffey and Livingston, Phase 1 Final Report.

Based on the previously described 20X increase in hydrogenation rate for the TRUGETTER formulation 20TS95E, the metal content of samples 20TS151B, -C and -D was reduced to allow more economical production of large TRUGETTER batches. In this instance, 20+ kg batches of polymer getter and getter pellets containing precious metal were produced for each of the sample formulations. As a consequence of reducing the catalyst content, the initial rate at ambient temperature for 20TS151C powder is only a factor of 6 greater than the original VIP formulation. Pellet forming reduced the initial rate of 20TS151C by 2X, allowing a net increase of 3X in hydrogenation rate at ambient temperature for pellets having about the same catalyst contents as VIP getter powder.

The measured capacity for 20TS151C pellets is 5.9 mol kg^{-1}, which is about 20 % less than for the VIP powder formulation (20TS151A). However, previous work at SRTC with the VIP formulation has demonstrated that hydrogenation rate at low temperatures, rather than capacity, is likely to be the limiting case in determining the mass of hydrogen getter required for use in the TRUPACT-II. Consequently, the 20 % decrease in capacity noted for the 20TS151C pellets should not cause a problem for the TRUPACT-II application. However, this fact points out the impact of extremely low temperatures on the use of hydrogen getters.

Operating Temperature Range

Theory

Reaction rate is an essential parameter for evaluating getters, but also a difficult parameter to measure as it changes dynamically as a function of temperature, hydrogen pressure, and percent loading as getter samples are tested. Significant variations in experimental parameters, procedures, or apparatus (e.g., geometry, mass, gas composition, etc.) may result in different observed reaction rates. Consequently, one of the best ways to test a getter is under the conditions of use or in the actual application. Because this is not practical at this stage of development, the following tests have been designed to provide a reasonable estimate of getter performance when deployed in the TRUPACT-II.

In general, hydrogenation and recombination rates accelerate with increasing temperature. These reactions are exothermic and entropically disfavored. These thermodynamics indicate that the equilibrium constant of the hydrogenation reaction will decrease with increasing temperature. Yet kinetically, a number of factors combine to yield increased rates. Increasing the temperature increases the diffusion rates of all the gases present, thus increasing the reaction rate of hydrogenation by bringing more hydrogen to the catalyst sites.

Where gas flow to the getter materials is restricted, localized depletion of the hydrogen can occur and produce an inert boundary layer that artificially lowers the observed reaction rates. Heat generated by getter operation will increase diffusion in both the surrounding headspace and within the getter material. The exothermic reaction may also proceed to a point that the temperature differential induces convection and brings more hydrogen to the reactive sites. Getter deployments that allow free flow of both hydrogen and the other atmospheric gases through the getter materials behave more predictably than when gas flow is restricted by the deployment geometry.

Increasing temperature of the hydrogen getter not only causes gases to diffuse more rapidly to the catalyst, but also increases the rate of unsaturated polymer diffusion. Although polymer getter materials are solids, the polymers that serve as hydrogen receptors are actually viscous liquids of high molecular weight. As the viscosity of the polymers drop with increasing temperature, unsaturated polymers can move to the catalytic sites more efficiently. The combination of all reactants moving more readily to the catalyst yields a dramatic increase in reactivity with increased temperatures. If the getter is not deployed in a manner that can reject the heat of reaction, the getter bed can get extremely hot. If the temperature of a polymer getter exceeds about 200 to 250 °C, the rubbers begin to polymerize further by cross-linking. This process rapidly increases the molecular weight and limits polymer diffusion to the catalyst, thus shutting down the hydrogenation reaction. This is an inherent safety mechanism in organic hydrogen getters because the chemical reactions shut down well below the ignition temperature of hydrogen/air mixtures or getter/air mixtures.

Getter materials that are supplied as free flowing powders are often poor heat conductors and are subject to non-uniform hydrogen absorption and heat build up depending on the degree of compaction. Excessive heat build up and non-uniform loading in getter deployments can be avoided by using pellets instead of powders, because pellets reject heat more easily than powders and allow free circulation of gas to help dissipate the heat of reaction. These same principles apply to heat generated by the recombination reaction.

Test description

Based on temperature extremes identified for TRUPACT-II normal conditions of transportation, the required operating temperature range for getters deployed in the TRUPACT-II extends from -20 ºF to +160 ºF (-29 ºC to +71 ºC). The rates of hydrogen removal from air by recombination and from nitrogen or vacuum by hydrogenation were measured at 50 % capacity and 5 % hydrogen (i.e., 38 Torr at 1 atm total pressure). The samples used in these tests were loaded to 50 % capacity based on the capacity measurements (SRS) provided in the preceding section of this report. Rate measurements were made at temperatures of -20, +23, +77 and +160 ºF. To achieve the lower temperatures, the samples were chilled for several hours following indication that the test vessel had reached the desired temperature before conducting the rate measurements. Samples tested at elevated temperature were also heated to constant temperature prior to making the addition of hydrogen. In these tests, the samples were placed in direct contact with the metal container rather than in a glass vial to increase thermal conductivity. Although the temperature of the sample was not measured directly, experience shows that the samples in direct contact with the test vessel cool and heat rapidly to the control temperature. The Arrhenius behavior of the getter materials for both air and inert atmosphere conditions is examined.

Hydrogen absorption rates were determined from pressure, volume, and temperature (PVT) measurements in a static system. These tests used 1.0 g of getter sample loaded into the small-scale test apparatus as described for capacity measurements. Rate measurements are made by first establishing the sample conditions for a given test (e.g., 50 % loading and +23 ºF) then adding a small, measured volume of the appropriate mixture of hydrogen to the sample at the desired pressure. Typically, this involved expanding a gas mix containing approximately 5 % hydrogen in air or nitrogen into the test vessel and recording pressure drop with time. The total pressure immediately after expansion into the test vessel was nominally 760 Torr at ambient temperature. In some cases, the measurement was made in vacuum with an initial hydrogen pressure between 35 and 40 Torr. The amount of hydrogen consumed in a single rate measurement was generally limited to less than 2 % of the sample’s capacity in order to minimize changes in the sample temperature and to limit the change in getter capacity. Once hydrogen was added to the sample container, pressure change over time was measured and recorded using instrumentation and data acquisition software previously described.

Test results

Figure 6 shows the impact of temperature on hydrogen removal as measured for 20TS151C pellets in vacuum. Note these pressure changes are plotted with time on a log scale because the time scales for these tests vary by over four orders of magnitude across this temperature range.

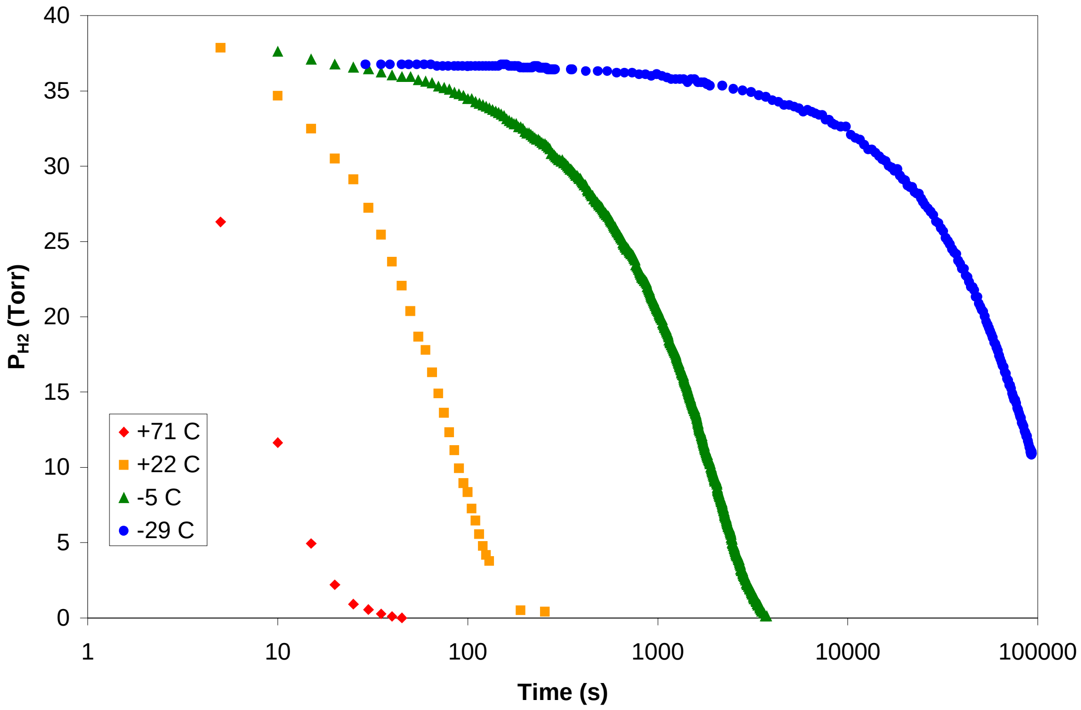


Figure 6. Effect of temperature on hydrogen absorption in vacuum for 20TS151C pellets.

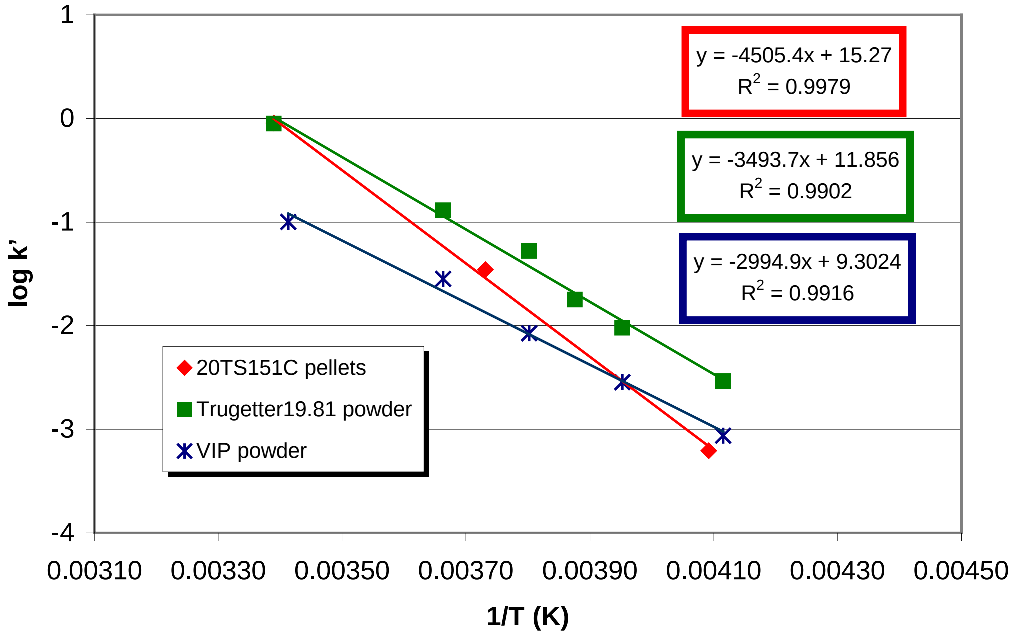


Figure 7. Arrhenius plots for polymer getter formulations at 0 % loading.

Figure 7 shows the Arrhenius behavior for several samples characterized at low hydrogen loading in vacuum. The data for 71 °C are not included in the linear fit in this and subsequent plots because the reaction rate does not consistently follow Arrhenius behavior. Even so, the reaction rates for all samples at 71 °C are significantly faster than ambient temperature as seen in Table 4. Notice that the slope of an Arrhenius plot (proportional to the activation energies) for the lab-scale TRUGETTER 19.81 powder and the VIP powder are similar, whereas the slope increases significantly for the production scale TRUGETTER 20TS151C pellets. Because of the increased activation energy, the hydrogenation rate for 20TS151C pellets at -29 °C is less than that for VIP powder, even though the rate at +24 °C is equivalent to that for TRUGETTER 19.81 powder. Additional measurements on 20TS151C powder (shown in Figure 8) demonstrated that this increase in activation energy was not the result of forming the powder into pellets. At this time the reason for the increase in activation energy is not clear.

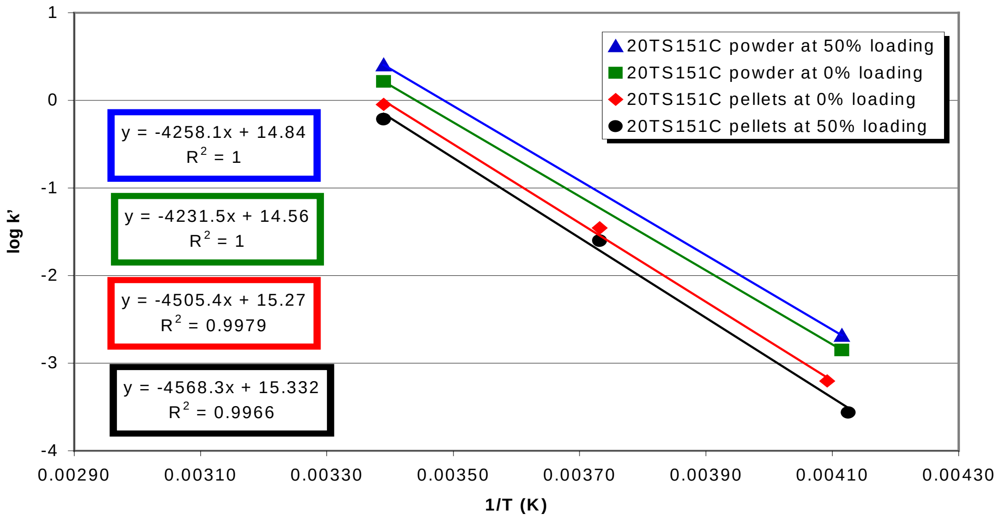


Figure 8. Arrhenius plots for polymer getter 20TS151C powder and pellets.

Figure 8 shows the Arrhenius plots for TRUGETTER 20TS151C powders and 20TS151C pellets at both 0 % and 50 % loading. The slopes of all four plots are quite similar indicating the activation energies are very similar for both powder and pellets. Typically, the rates of hydrogenation decrease with getter loading, as can be seen for the 20TS151C pellets at 0 % and 50 % loading. However, the rates measured for 20TS151C powder were about 1.5 times faster at 50 % loading than at 0 % loading. This result was unexpected and should be investigated further. Because of this the rate for the powder was about 2 times faster than for the pellets at 0 % loading, but about 6 times faster at 50 % loading across the temperature range of 24 °C to –29 °C.

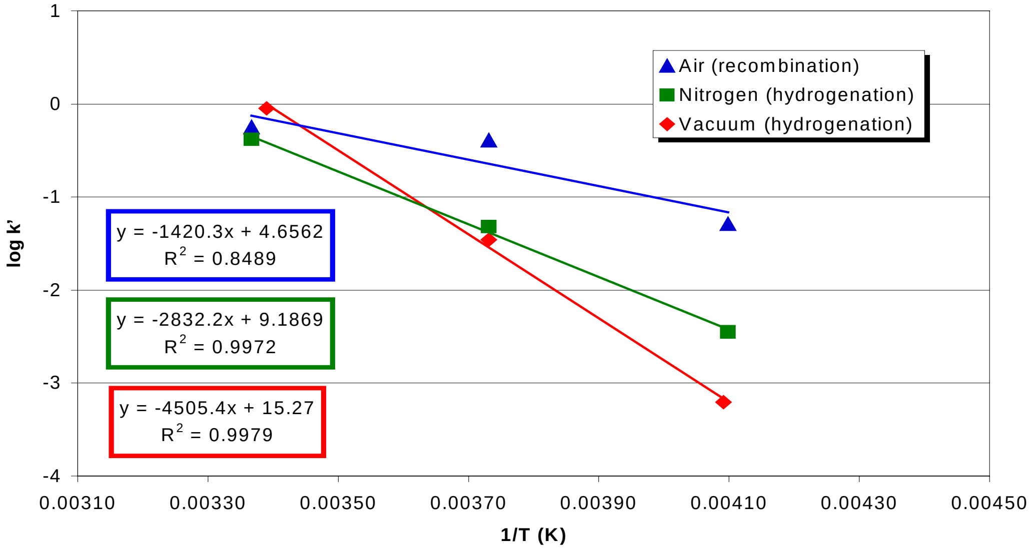


Figure 9. Arrhenius plots for 20TS151C pellets in air, nitrogen, and vacuum at 0 % getter loading.

Figure 9 compares the Arrhenius plots for hydrogen removal from vacuum, nitrogen and air. Note that the temperature dependence of recombination is much less than that for hydrogenation. In this series of tests, the rate of hydrogenation in nitrogen at –29 °C was almost six times faster than the corresponding rate in vacuum. However, these data have yet to be confirmed and are suspect because results for other getter formulations tested to date indicate little or no difference between rates measured in vacuum and in nitrogen. Table 4 provides a summary of the reaction rates for various conditions described above.

Table 4. Summary of Rate Data for 20TS151C Pellets as a Function of Temperature.

	Rate of Hydrogen Removal (mol s^{-1} kg^{-1} at $2x10^{-3}$ M H_2)			
Temperature ^oC	In Air	In Nitrogen 0% loading	In Vacuum 0% loading	In Vacuum 50% loading
71	1.42E-03	—	1.90E-02	3.62E-03
24	1.15E-03	8.59E-04	1.86E-03	1.26E-03
-5	8.41E-04	9.94E-05	7.20E-05	5.18E-05
-29	1.06E-04	7.30E-06	1.29E-06	5.60E-07

Based on these rate measurements, the mass of TRUGETTER required to meet the 1.2 x 10^{-5} mol s^{-1} hydrogen generation rate for the TRUPACT-II can be calculated. The minimum mass is calculated by dividing the required rate by the observed rate for TRUGETTER under the specified conditions. For example, the mass of getter required to meet the specified rate at –29 °C using TRUGETTER at 50 % loading in vacuum is 1.2 x 10^{-5} mol s^{-1} divided by 5.60 x 10^{-7} mol s^{-1} kg^{-1} or 21.4 kg. Based on the data in Table 4, this is the maximum quantity of getter needed to maintain the headspace gas content of the TRUPACT-II below 5 % hydrogen because the maximum quantity of getter is required at the minimum temperature.

A second temperature effect evaluated as part of the consolidated test plan is the long-term impact of elevated temperature on getter performance. To evaluate the impact of exposure to elevated temperature for an extended period, samples were stored for up to 64 days at +160 ºF (71 °C) in air, then hydrogen absorption rates and capacities for the heat-aged samples were measured.[21] The impact of long-term heating on hydrogenation rate is shown in Figure 10. These tests were run in vacuum at ambient temperature, and the calculated rates are the average rates for pressure drop from 10.0 to 9.8 Torr.

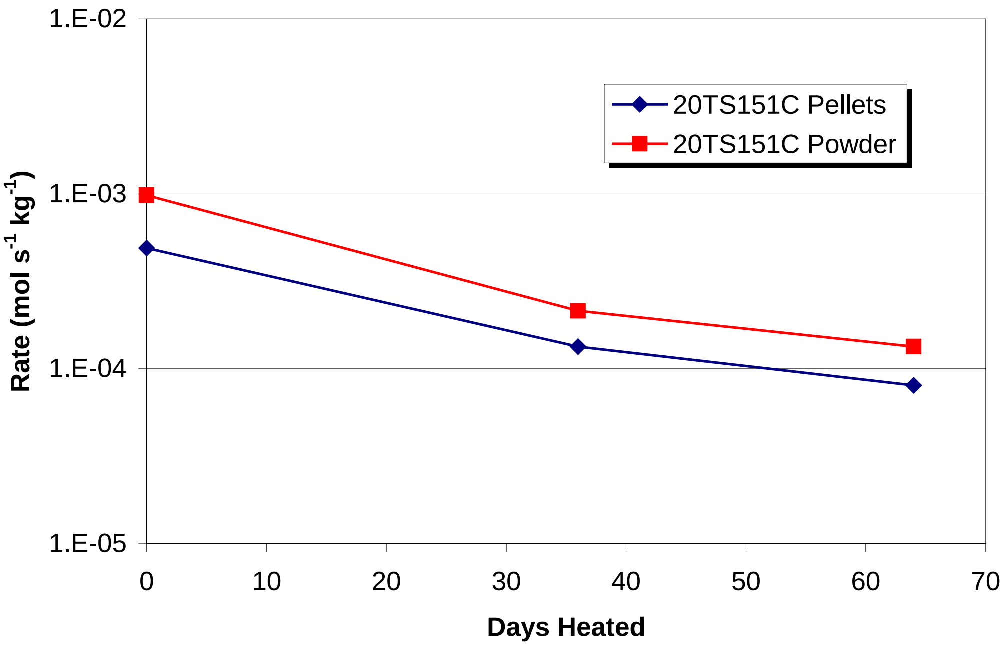


Figure 10. Effect of long-term heat aging on TRUGETTER hydrogen absorption rate in vacuum at 0 % loading and 10 Torr hydrogen.

---

[21] These tests were conducted at SNL. The test protocol is described in Attachment 3.

Figure 11 shows the effect of extended storage at 71 °C on the measured hydrogen capacity, and Table 5 summarizes the impact of elevated temperature on both rate and capacity. After 64 days of heating at 71 °C, the rates for powder and pellets decreased by factors of 6.1 and 7.3, respectively. The capacities for both materials decreased by about 10 %.

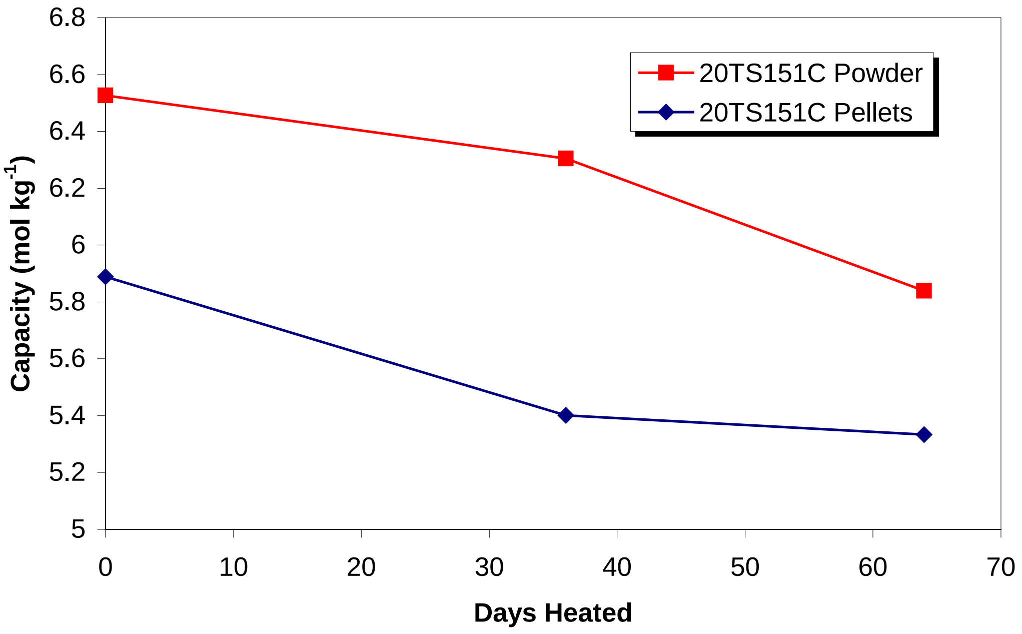


Figure 11. Effect of long-term heating on capacity of TRUGETTER.

Table 5. Evaluation of Rate and Capacity Following Storage at 71 °C.

	20TS151C Pellets		20TS151C Powder	
Days Heated	Rate* (mol s^{-1} kg^{-1})	Capacity (mol kg^{-1})	Rate* (mol s^{-1} kg^{-1})	Capacity (mol kg^{-1})
0	4.91E-04	5.89	9.82E-04	6.53
36	1.34E-04	5.40	2.14E-04	6.30
64	8.04E-05	5.33	1.34E-04	5.84

*Rates were measured in vacuum at 0 % loading and 9.8 to 10.0 Torr hydrogen.

One possible explanation for the observed decreases in reaction rate and capacity is cross-linking of the rubber molecules to form higher molecular weight species that have higher viscosities and are less mobile. SNL attempted to identify cross-linking in thermally aged getters that were both slowly and rapidly hydrogenated. No evidence of cross-linking was evident by ^{13}C MAS NMR (Conditions: solid getter ^{13}C at 150.92 MHz, single pulse acquisition, 16 kscans, 10 s recycle delay, spinning 9.5 kHz, 298 K, TPPM ^{1}H decoupled.).

An alternate explanation for the decrease in hydrogenation rates and capacities with long-term heating is a decrease in surface area for the getter materials that results from intrusion of rubber into micropores. A modest decrease in surface area was measured for some aged samples (Table 6). It is difficult to make firm conclusions from this data.

Table 6. Effect of Long-Term Heating on Polymer Getter Surface Area.

Sample ID	Surface Area Unheated (m^2/g)	Surface Area Thermal Aged (m^2/g)
20TS95E (High Activity)	7.81	7.82
20TS28I (High Activity)	5.28	4.93
VIP Getter (Lower Activity)	0.26	0.22

Additional evaluation of this effect is needed to determine how to adjust the mass of getter required for use in the TRUPACT-II to account for the impact of heat aging. The impact of heat aging would require no additional getter mass if evaluating getter requirements at normal or elevated temperatures; however, at the low temperature extremes the reduction in rate may become significant.

New Polymer Getter Pellets

To address the increase in activation energy observed for the 20TS151C formulation, a second series of getter formulations (series 25TS78) were produced at the process-scale and subsequently formed into pellets by a process different than that used by Engelhard. This alternate process did not require the addition of binding agents to aid pelletization. The absolute density of 25TS78 powder is 1.2 g/cc whereas loose powder has a density of 0.4 g/cc. Absolute pellet density is 1.3 g/cc whereas loose pellets pack at 0.6 g/cc. The capacity and effect of temperature on rate for pellets produced by this process were also evaluated during Phase 2. The capacity and rate data for one formulation (25TS78B pellets) are summarized in Table 7 along with comparable data for 20TS151C pellets. The Arrhenius behavior of both these materials is compared in Figure 12. The increased capacity for 25TS78B pellets can be attributed to the absence of the binding agents used in 20TS151C pellets, thus allowing for increased rubber content. As seen in Figure 12, the slope of the Arrhenius plot for 25TS78B pellets is much less than for 20TS151C pellets and is, in fact, similar to that for VIP and TRUGETTER 19.81 (Figure 7). As a result, the two pellet formulations have equivalent rates at ambient temperature, but the rate for 25TS78B is about 25 times faster than for 20TS151C at -29 °C. With this significant increase in rate at low temperature, only about 0.83 kg of 25TS78B pellets would be required to meet the specified rate at 5 % (38 Torr) hydrogen.

Table 7. Comparison of Capacity and Rate Data for TRUGETTER Pellets

Getter Formulation	Capacity (mol kg^{-1})	Rate (mol s^{-1} kg^{-1})		
		+24 °C	-5 °C	-29 °C
20TS151C	5.84	1.26E-03	5.18E-05	5.60E-07
25TS78B	6.31	1.25E-03	—	1.44E-05

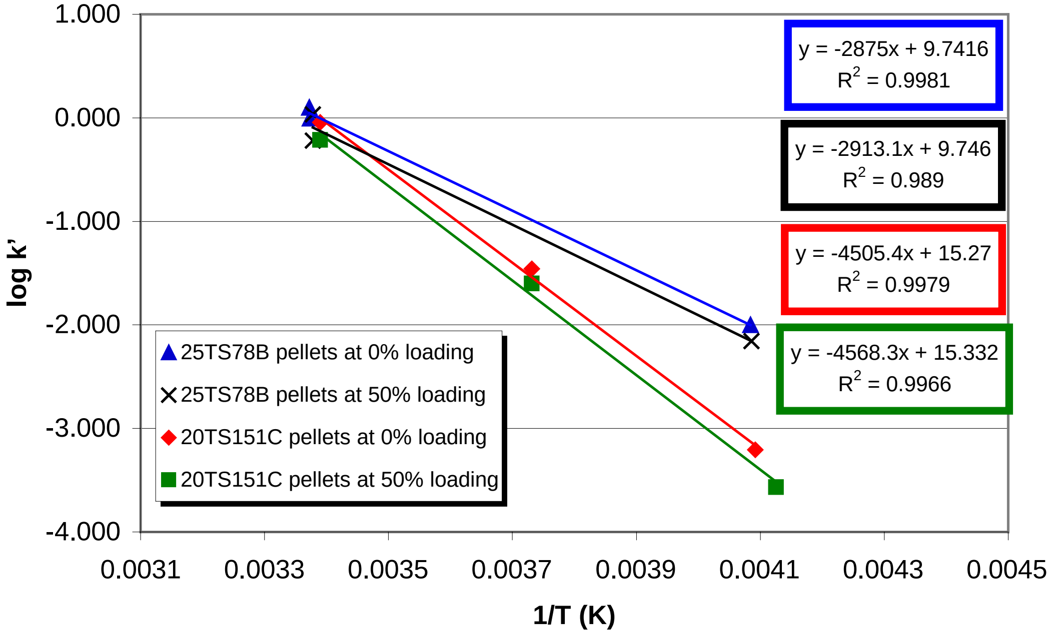


Figure 12. Arrhenius plots for TRUGETTER formulations 25TS78B and 20TS151C.

Poisons

Theory

Catalysts used as part of hydrogen getter formulation are subject to poisoning by some gases and vapors that may be present in the TRUPACT-II. The most reactive gases (e.g., H2S, R–SH) can combine with the catalyst to stop hydrogenation. Other reactive gases (e.g., CO, HCN) bind with the catalyst reversibly, slowing hydrogen uptake unless they are removed. Consequently, hydrogen getters must be designed with sufficient excess rate for anticipated loss of reactivity due to poisons or may be co-deployed with materials that separately sorb or filter the poisons before they affect the catalysts' function. In some instances, the getter formulation is sufficient to prevent damage to the catalyst or the getter may be coated to selectively remove poison vapors as demonstrated by the INEEL/LANL getter team.[22] Numerous potential poisons have been identified for TRUPACT-II as part of the Statement of Work and this list has been narrowed to a manageable number of representative poisons in the consolidated test plan.

The focus of the consolidated test plan is to screen the getter materials against various vapors or gases anticipated in the TRUPACT-II that may act as getter "poisons". As mentioned above, poison vapors or gases may impede the operation of a hydrogen getter in several ways, but measuring hydrogen removal rates and capacities in the presence of each potential poison is expected to capture the impact produced by each of these mechanisms. The consolidated test plan requires getter evaluation against several classes of potential poisons. This is accomplished by selecting a representative material from each class for use as a poison candidate. In the case of halogenated organic compounds, previous work has demonstrated that the more highly chlorinated compounds (such as carbon tetrachloride) are the most aggressive poisons. This evaluation primarily addresses the impact of single poisons and not combinations of poisons. However, the consolidated test plan does address the potential for synergistic effects by using a mixture of the two worst poisons identified during the screening tests for individual poisons.

Test description

Poison-screening tests were conducted by measuring the hydrogen removal rate with and without the potential poison vapors or gases as part of the gas composition. Each test was conducted using 1000 ppm (vol/vol) of the selected vapor or gas.[23] Tests of the potential poison compounds were conducted under both hydrogenation and recombination reaction conditions. These poison tests were conducted principally in the SRTC large volume apparatus, which allows for an approximate 50X increase in the volume to mass ratio anticipated for the TRUPACT-II. In these tests, a 0.5 g sample of getter was exposed to 2.42 L of gas containing 0.76 ± 0.05 Torr of poison vapor or gas, which is equivalent to a poison concentration of 1000 ppm at a total pressure of 1 atm. However, the volume to mass ratio was approximately 4840 L kg^{-1}, or about 50 times that anticipated for a getter deployed in the TRUPACT-II ICV (i.e., 25 kg in 2450 L). Consequently, these tests are believed to be conservative evaluations of TRUGETTER's capacity to withstand the impact of poisons.

---

[22] INEEL/EXT-01-01325, Improved Hydrogen Gas Getters for TRU Waste, Mark Stone, Michael Benson, Chris Orme, Eric Peterson and Eugene Mroz, Idaho National Engineering and Environmental Laboratory, October 2001.

[23] IT Corporation, "Parameters for Testing Impacts of VOCs as Poisons on Hydrogen Getter Performance," April 2001.

The compounds selected for screening as potential poisons are highlighted in Table 8 using bold formatting. These poisons were selected from the list of optional poisons provided in the consolidated test plan and include hexane, toluene, acetone, methanol, carbon tetrachloride and carbon monoxide.

Table 8. Potential Poisons for Getter Screening.

Represented Class	Selected Compound(s)
Aliphatic	**hexane**
Aromatic	**toluene**, benzene
Ketone	**acetone**, methyl ethyl ketone
Alcohol	**methanol**
Chlorinated organic	**carbon tetrachloride**, 1,1,1-trichloroethane, chloroform, methylene chloride, trichloroethene, tetrachloroethene
Inorganic gases	**carbon monoxide**, hydrogen chloride,

Each test was run using 0.5 g of sample placed in a wire basket scaled geometrically to resemble a 55-gallon drum (approximately 1:33 scale). Three photos of this apparatus are included in Attachment 7. The appropriate gas mix was made using services connected to the gas manifold for air, nitrogen, and hydrogen. Poison gases and vapors were added by connecting additional vessels to the manifold. The data in Table 9 are provided to demonstrate that each of the poison compounds have much greater vapor pressures at ambient temperature than required to provide the 1000 ppm concentration selected for these tests.

Table 9. Vapor Pressures of Potential Poisons used in Screening Tests.

Compound	Vapor Pressure at 20 °C (Torr)
Hexane	> 100
Toluene	22
Acetone	176
Methanol	96
Carbon tetrachloride	100
Carbon monoxide	NA*

* CO is a gas and was added from a standard gas mixture containg 1 % CO.

Test results

In Figure 13A, the amount of hydrogen absorbed by TRUGETTER 20TS151C pellets from a nitrogen atmosphere is plotted against time. This graph shows the minimal impact that hexane, toluene, acetone, carbon tetrachloride and methanol have on getter performance when the getter is packaged with zeolite as previously described. In previous testing, SRTC determined that carbon tetrachloride has a measurable impact on polymer getter if tested without zeolite present.

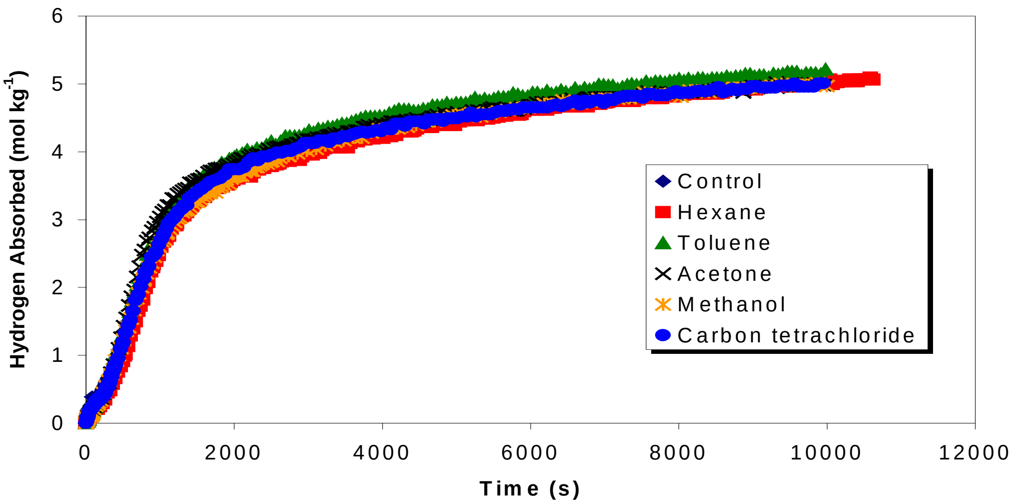


Figure 13A. Effect of poison vapors on 20TS151C pellets deployed with 13X zeolite.

The presence of zeolite does not mitigate the poison effect of carbon monoxide, as shown in Figure 13B along with the results for carbon tetrachloride poisoning when no zeolite is used.

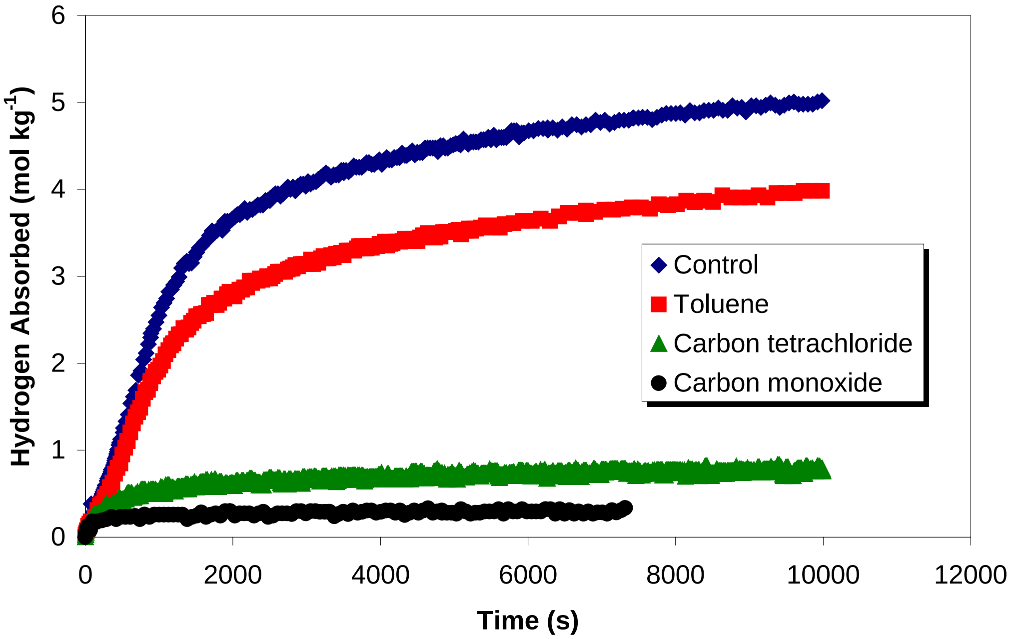


Figure 13B. Effect of poison vapors and gases on 20TS151C pellets with no zeolite.

To mitigate the impact of carbon monoxide, a commercial reagent called HOPCALITE was used to convert carbon monoxide to carbon dioxide. Figure 14 shows the improvement in getter performance with 33 % HOPCALITE added to the zeolite to prevent carbon monoxide poisoning. HOPCALITE has been used for many years for this purpose in applications important to human health and safety (e.g., respirator cartridges and underwater breathing apparatus). This same mixture was used when testing the combined effects of the two worst poisons to evaluate potential synergistic effects. The results of this test combining 1000 ppm of both carbon monoxide and carbon tetrachloride are also shown in Figure 14.

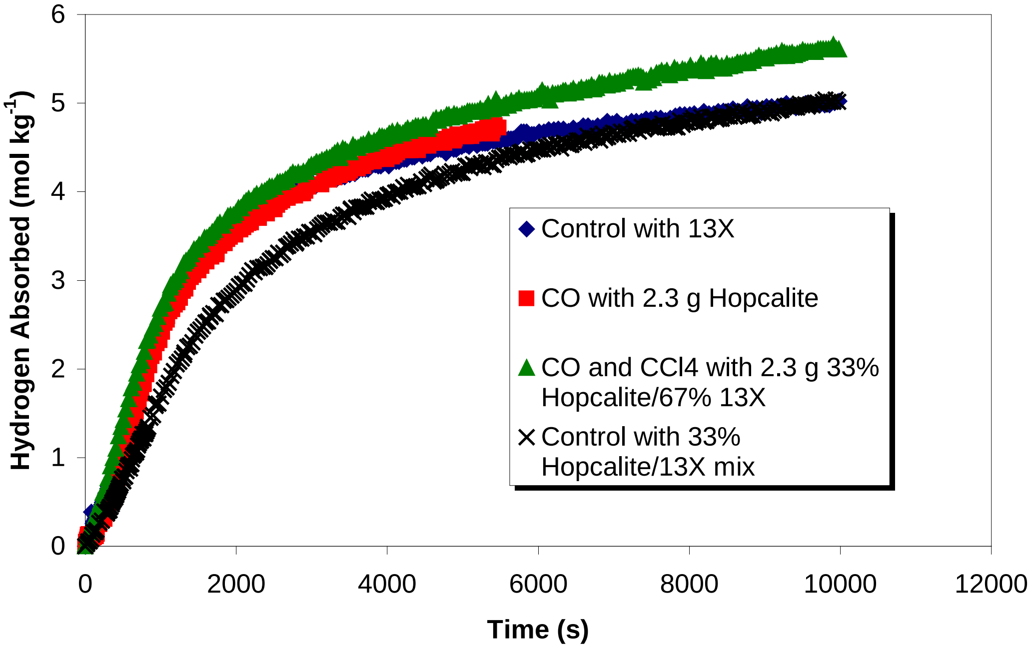


Figure 14. Effect of CO and CCl_4 on 20TS151C pellets combined with Hopcalite and zeolite.

Results for both hydrogenation and recombination tests run in the presence of 1000 ppm of poison are summarized in Table 10. For these poison tests enough hydrogen was added in a single addition to load the sample to capacity with an excess of 10 to 25 Torr of hydrogen remaining. The initial hydrogen pressure was selected such that approximately 38 Torr remained at the point when the getter sample was 50 % saturated. To determine the rate of hydrogen removal, the amount of hydrogen absorbed (mol kg^{-1}) was calculated and plotted versus time (s). Then, the rate at 50 % loading and 38 Torr hydrogen was obtained from the slope of a linear fit of this data in the region between about 2.8 mol kg^{-1} (48 % loading) and 3.1 mol kg^{-1} (52 % loading) (Figure 15). For recombination measurements where capacity is not actually consumed, these measurements reflect the rate of recombination following removal of an equivalent amount of hydrogen.

Table 10. Effect of Poison Vapors or Gases on Rate at 50 % Capacity.

Poison	Hydrogenation Initial P_{H2} (Torr)	Rate in N_2 (mol s^{-1} kg^{-1})	Recombination Initial P_{H2} (Torr)	Rate in Air (mol s^{-1} kg^{-1})
None (control)	50	1.65E-03	50	5.27E-03
None (control)	---	---	25	3.77E-03
Hexane	50	1.24E-03	25	3.67E-03
Toluene	50	1.83E-03	25	3.44E-03
Acetone[24]	50	1.86E-03	50	6.67E-03
Methanol	50	1.29E-03	25	2.75E-03
Carbon tetrachloride	50	1.45E-03	50	8.44E-03
Carbon monoxide	50	1.44E-03	=	=
Carbon monoxide/carbon tetrachloride	50	1.32E-04	25	3.67E-03

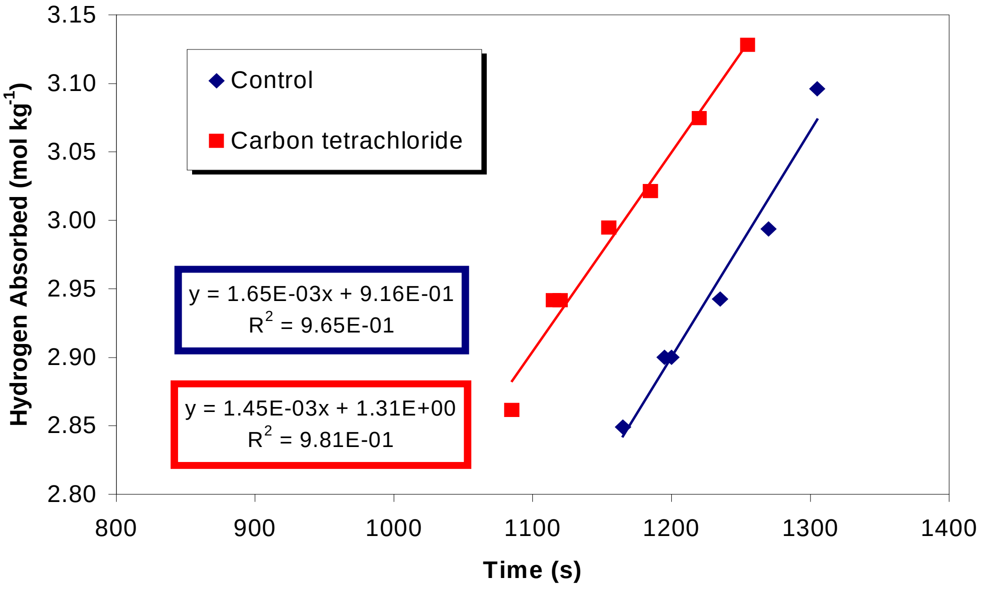


Figure 15. Example of data used to calculate rate of hydrogen removal for poison tests in large-scale test apparatus.

---

[24] Acetone may be reduced to 2-propanol on the catalyst surface in the presence of hydrogen. This reaction does not significantly impact calculation of the getter capacity.

These poison test results demonstrate that the impact of each poison is mitigated by the appropriate getter assembly design even when present at 50X the volume-to-mass ratio anticipated for use in the TRUPACT-II.

Additional poison screening tests were conducted in the small-scale test vessels in order to evaluate the impact of carbon tetrachloride the rates across the full temperature range (–29 ºC to +71 ºC). In these tests the rates of hydrogen removal from vacuum, nitrogen and air in the presence of 1000 ppm poison vapor (i.e, 0.76 Torr) were measured as a function of temperature for comparison with the rates measured without poison. The rate data with and without poison are summarized for 20TS151C pellets in Figure 16 and Table 11. The presence of 1000 ppm carbon tetrachloride had no significant impact on 20TS151C pellets across the full temperature range tested.

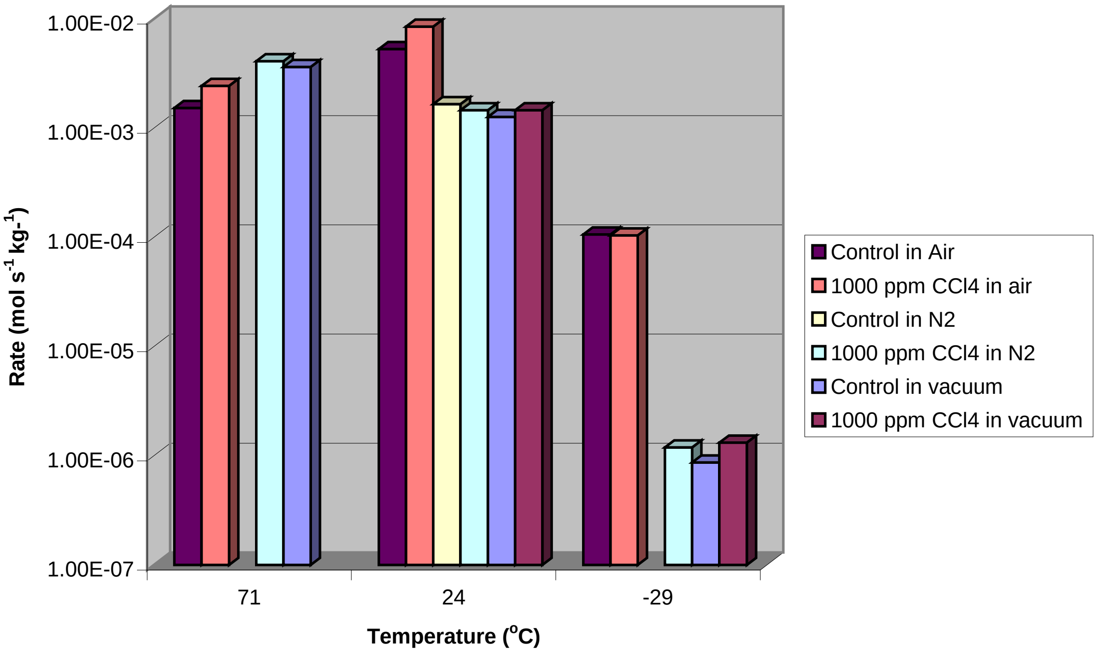


Figure 16. Hydrogen removal rate for 20TS151C pellets with and without 1000 ppm carbon tetrachloride.

Table 11. Rate Data for 20TS151C Pellets as a Function of Temperature with and without Poison Present

Atmosphere	Temperature (°C)	Rate at 50% Loading ($mol\ s^{-1}\ kg^{-1}$)	
		Control	Poison (1000 ppm CCl_4)
Vacuum	+71	3.62E-03	—
	+24	1.26E-03	1.45E-03
	-29	8.63E-07	1.32E-06
Nitrogen	+71	—	4.08E-03
	+24	1.65E-03	1.45E-03
	-29	—	1.19E-06
Air	+71	1.52E-03	2.43E-03
	+24	5.27E-03	8.44E-03
	-29	1.06E-04	1.04E-04

The build-up of water on a getter material could also provide a potential mechanism to "poison" the getter response. To evaluate this effect for TRUGETTER, both pellets and powders were stored in a sealed container at 100 % relative humidity for approximately one month to measure water uptake at ambient temperature. A 1.0 g sample (weighed to the nearest 0.1 mg) of each material was placed in a 4 dram glass vial and the total weight recorded. The two sample vials, an empty control vial, and a vial of water, were placed into a plastic screw-cap container, which was then sealed. The control and sample vials were removed at various intervals and weighed to track moisture uptake. The results of this test are shown in Figure 17.

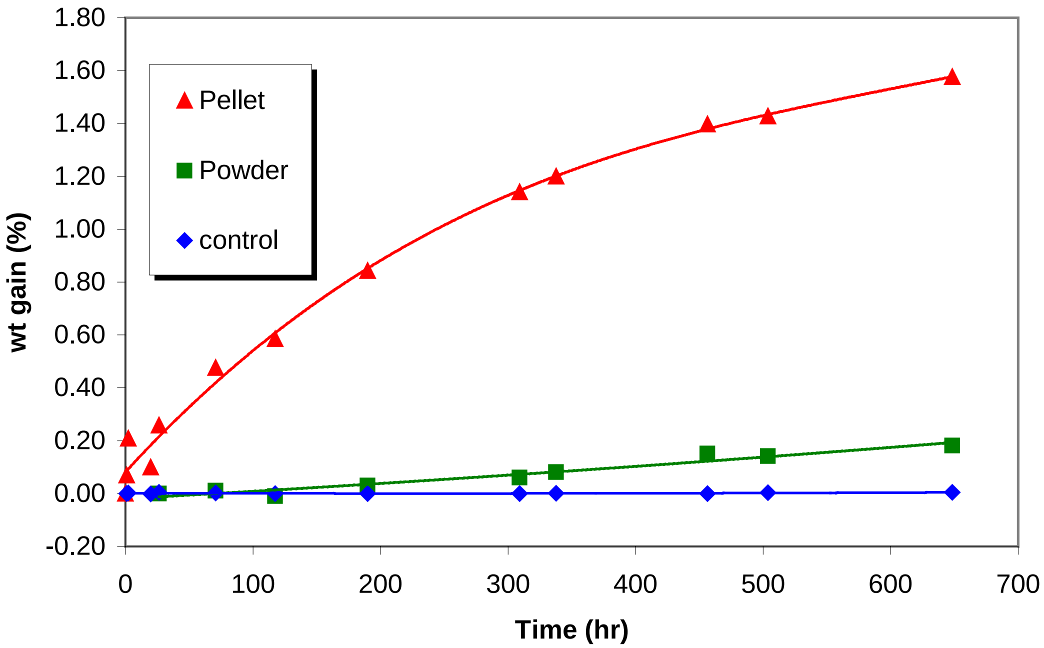


Figure 17. Water adsorption for 20TS151C pellets and powder.

The increased water uptake for pellets relative to powder results from binders used by Engelhard in the pelletization process and provided the initial impetus to evaluate additional means for pellet production as discussed in the previous section on operating temperature.

The rate of hydrogenation showed little or no impact due to this moisture uptake when measured at ambient temperature. Nevertheless, codeployment with a zeolite is expected to adsorb any water present in the TRUPACT-II as well as water generated by the recombination mechanism. It has been previously noted that the amount of water generated by recombination of all hydrogen generated during 60 days of storage can be no more than 1.1 L. Additional evaluation of water generation due to recombination will be addressed under the discussion of free liquids to follow.

Pressure

The impact of ICV pressure on getter function was evaluated by measuring rates of hydrogen removal from nitrogen and air at total pressures of 0 psig and 50 psig with a 1.0 g sample of getter loaded to 50 % capacity. Mixtures of 5.0 % hydrogen in nitrogen and 4.8 % hydrogen in air were each introduced into the test vessel at initial pressures of either 0 psig or 50 psig. The rate of hydrogen removal at a hydrogen partial pressure of 38 Torr (0.0021 mol L^{-1}) was calculated from the observed change in pressure with time as previously described. (This corresponds to the rate for 5 vol % hydrogen at 0 psig and 1 vol% hydrogen at 50 psig.) The observed pressure drop in air was divided by 1.5 to correct for the simultaneous removal of oxygen due to recombination. The calculated rates are given in Table 12. The hydrogen removal rates at 50 psig are about 1.5 to 2 times less than at 0 psig.

Table 12. Effect of Total Pressure on Rate of Hydrogen Removal by 20TS151C Pellets at 50 % Getter Loading.

Total Pressure (psig)	Fill Gas	Rate of H_2 Removal at 0.002 M H_2 (mol s^{-1} kg^{-1})
0	N_2	7.44E-04
50	N_2	3.74E-04
0	air	1.37E-03
50	air	1.03E-03

Free Liquids

Theory

Liquid water can affect the operation of getters. Polymer getters were originally invented because the DEB-type getters become wet and inactive when they are exposed to excess liquid water or volatilizing steam. The hydrophobic nature of the rubbers used in the polymer getters prevents the catalyst from becoming wet and allows years of service in dripping wet or steam atmospheres.[25,26] Polymer getters even work under water, but their reactivity is limited to the diffusion rate of hydrogen through the surrounding water. Similarly, ice has little effect on the function of the hydrogen getter except when it becomes a barrier to hydrogen diffusion into the getter bed.

If the getters are warmer than their surroundings (as is often the case from the heat of reaction), any water formed may condense on cooler surfaces elsewhere in a sealed vessel. The engineered form of the polymer getter will incorporate activated molecular sieves (zeolite) to scavenge

---

[25] Shepodd, T. J.; Daniel, A. R. *New Organic Hydrogen Getters for Use in Vacuum Insulated Tubulars and Heat Pipes*; SAND95-8256; Sandia National Laboratories: Livermore, CA, November 1995

[26] Shepodd, T. J.; Tichenor, M. S. *Organic Hydrogen Getters for the use in Heat Pipes*; SAND99-8218; Sandia National Laboratories: Livermore, CA, April 1999.

water formed in the recombination reaction so that it will not migrate and condense as liquid elsewhere in the TRUPACT-II.

Test description and results

A sample consisting of 0.51 g of 20TS151C pellets and 2.0 g of 13X zeolite was placed in a sample container and sealed in air. The total volume of the container and associated tubing was 62.3 mL, for a volume to mass ratio of 122. This is approximately equal to the ICV volume to getter mass ratio anticipated for the TRUPACT-II. Sufficient hydrogen was added to the sample container to consume all of the oxygen by recombination, thus forming about 0.02 g of water (or 4 % of the getter weight). The sample container was evacuated briefly to minimize removal of water vapor, and the hydrogen absorption rates in vacuum at 0 % and 50 % getter loading were measured in the usual manner. The calculated absorption rates at a hydrogen pressure of 38 Torr (0.002 mol L^{-1}) were approximately 35 % lower than those measured for a control. The results of these tests are summarized in Table 13. This difference is within the estimated overall uncertainty for rates measured in these tests.

Table 13. Effect of Water of Recombination on 20TS151C Pellets.

Condition	Getter Loading (%)	Rate (mol s^{-1} kg^{-1})
dry (control)	0	1.86E-03
	50	1.26E-03
adsorbed water	0	1.21E-03
	50	7.95E-04

Reversibility

Reversibility applies to the potential of some hydrogen absorbers to release hydrogen at elevated temperature. Polymer hydrogen getters are not subject to reversible release of hydrogen at TRUPACT-II temperatures because the hydrogen is chemically reacted with oxygen or an unsaturated organic polymer to form stable covalent bonds. However, a simple test of reversibility was conducted as required by the consolidated test plan. This was accomplished by loading a sample of getter to full capacity, then heating the sample under vacuum to determine if hydrogen was released or if the sample had significant out gassing.

In order to implement this test, a 0.25 g sample of getter pellets was sealed in a small-scale test vessel and evacuated for approximately 1 hour to degas the sample. Next, the sample was heated to 71 °C for about 50 min in the sealed container while recording the vessel pressure. After heating, the sample was reacted with hydrogen until about 90 % hydrogenated. This amount of hydrogen in the small-scale test vessel would exhibit a pressure of about 400 Torr at ambient temperature. Finally, the hydrogenated sample was heated to 71 °C again for about 50 min in the sealed container to compare the vessel pressure with that for the un-hydrogenated sample when heated. Figure 18 shows the results of this test. Note that no additional pressure rise upon heating was noted for the hydrogenated sample, thus indicating no release of hydrogen at the test temperature.

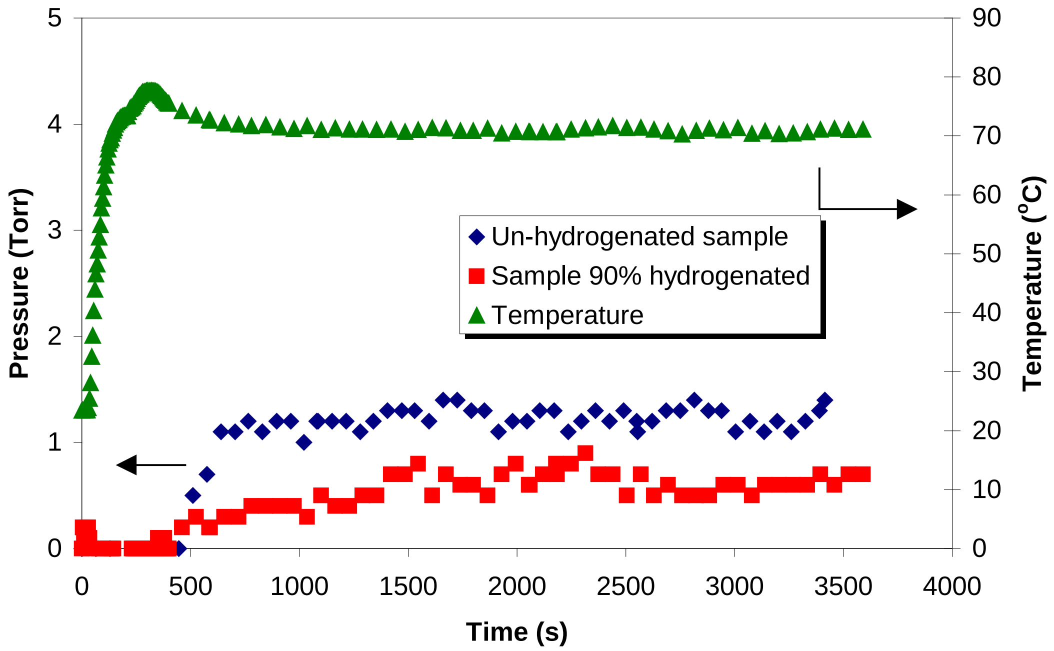


Figure 18. Testing reversibility of hydrogen absorption for 20TS151C pellets.

Radiation Effects

Theory

Ionizing radiation damages polymer hydrogen getters by generating reactive radicals that cause cross-linking and other detrimental reactions. The getters are formulated with radical scavengers both as anti-oxidants and as carbon-based radical scavengers. Exposure to radiation doses much higher than anticipated in the TRUPACT-II causes a minimal decrease in the reactivity of the polymer getters.

The current preferred alternative for deployment of TRUGETTER is installation in the ICV where significant radiation dose is not anticipated. Samples of TRUGETTER were exposed to 2.5 x 10^4 rad of gamma radiation from a Co-60 source. This is at least six times greater than the dose a hydrogen getter would ever encounter when exposed for 60 days to the maximum limit of

200 mrem hr^{-1} for contact handled TRU drums. The maximum dose estimated for a getter used in transportation of contact handled TRU waste is only about 4.0 x 10^3rem (i.e., 14 drums x 200 mrem hr^{-1} x 24 hr day^{-1} x 60 day = 4032 rem). This is equivalent to about 4.0 x 10^3 rad of gamma dose, which should have little or no effect on polymer getter materials.

With some possibility of using hydrogen getters for remotely handled waste forms, the radiation dose could potentially increase to about 1 R hr^{-1} at the surface of each drum.[27] The cumulative dose to a hydrogen getter under these conditions could rise to about 2.0 x 10^4 rad over the course of 60 days. Consequently, samples were tested at this radiation dose to demonstrate robust performance following irradiation.

Test description

A 1.0 g sample of getter pellets was exposed to a radiation dose of 2.5 x 10^4 rad in a cobalt-60 gamma source. The hydrogen absorption rate and capacity of the sample were then measured in the usual manner for comparison with an unirradiated control. Figure 18 shows the loading curves for the irradiated and unirradiated samples. The capacity of the irradiated sample after 75,000 s was 5.72 mol kg^{-1}, or 2.0 % lower than that of the control after the same time. The hydrogen absorption rate in vacuum at 50 % loading was 6.49x 10^{-4} mol s^{-1} kg^{-1} compared to 1.26 x 10^{-3} mol s^{-1} kg^{-1} for the control. Similar results were obtained for an irradiated sample of 20TS151C powder. The results are summarized in Table 14. Based on these data, no significant radiation effects are anticipated for a getter deployed in the TRUPACT-II ICV.

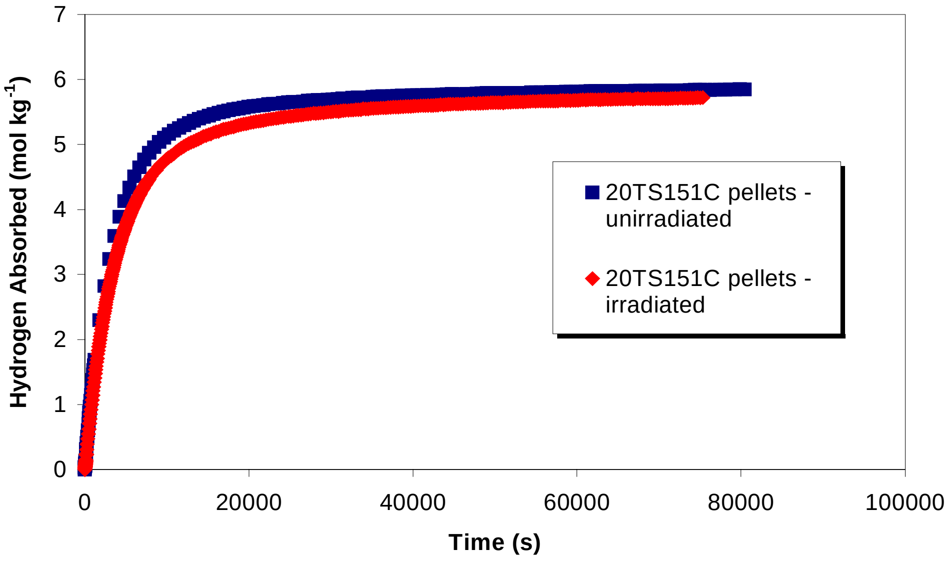


Figure 19. Effect of a gamma irradiation on TRUGETTER capacity.

---

[27] Personal communication with Brent Daugherty, Savannah River Site.

Table 14. Summary of capacity and rate data for irradiated and unirraditated TRUGETTER samples.

Sample	Capacity ($mol\ kg^{-1}$)		Rate ($mol\ s^{-1}\ kg^{-1}$)	
	Unirradiated	Irradiated	Unirradiated	Irradiated
20TS151C pellets	5.84	5.72	1.26E-03	6.49E-04
20TS151C powder	6.72	6.45	5.25E-03	2.45E-03

Temperature Effects

The hydrogenation reaction is exothermic and the amount of heat generated is about 125 kJ mol^{-1} of double bonds hydrogenated. This value is approximate because the 1,1- and 1,2- (cis or trans) substituted double bonds have 3 separate heats of reaction upon hydrogenation. The polybutadiene-based polymers used in getters have a distribution of all 3 types of double bonds. The recombination reaction generates about 250 kJ mol^{-1} (Actually 242 kJ mol^{-1} gas, or 286 kJ mol^{-1} liquid). The heat of adsorption for water on a molecular sieve is approximately 75 kJ mol^{-1}.

The thermal output of TRUGETTER has been estimated under the worse-case conditions. During recombination of hydrogen and oxygen, more heat is generated than for the hydrogenation reaction as described above. In the proposed getter assembly, which includes a zeolite to adsorb any water as it is produced, the heat of adsorption for water on a molecular sieve is added to the heat of formation for water to calculate the total thermal output. This calculation assumes that hydrogen is generated at the maximum rate and both reactions proceed simultaneously. The calculated heat output values are shown in Table 15. Consequently, the combined thermal output for the recombination reaction and adsorption on a molecular sieve is about 4.3 W. Based on this value the TRUPACT-II payload could be expanded to nearly 90 % of the authorized 40 W maximum.

Table 15. Thermal Output for TRUGETTER.

Reaction	Maximum Heat Generation (Watts)
Recombination	3.4
Adsorption of water on mol. sieve	0.9
Hydrogenation of TRUGETTER	1.5

Structure/Shape

Not required for Phase 2 testing.

Compatibility

The components used in developing the getter materials are similar to those currently transported in the TRUPACT-II. Packaging of the getter as part of a deployment effort is expected to further address this issue. The consolidated test plan does not require any testing of materials compatibility. However, there are no known compatibility issues associated with the use of polymer hydrogen getter or other materials that are described as potential components of the getter assembly.

Cost

Cost evaluation is not required by the consolidated test plan. However, the investigators recognize that the cost of implementing hydrogen getters is an important consideration for the overall success of this program. Toward this end, an evaluation of precious metal recycling has been conducted by Engelhard and shown to have minimal losses on the order of 0.05%. Consequently, the precious metal in TRUGETTER can be recycled to greatly reduce the overall cost of getter production.

Active vs. Passive

The getter materials used in the current programs are passive and require no active components as part of their function. Evaluation of the getter materials, following the consolidated test plan, also demonstrates that the hydrogen getters are passive. Furthermore, no activation steps are necessary prior to use of the polymer hydrogen getter or other materials that are described as potential components of the getter assembly.

Experimental Results for DEB Getters

As part of the Phase 2 test program, each team of investigators (i.e., INEEL/LANL team and SNL/SRTC team) was directed to evaluate the getter material(s) being developed and tested by the other team. The purpose of this sample exchange program was to provide a clear basis for comparison of each getter material by having each material evaluated under the different testing protocols used by each team (i.e., dynamic or static tests). The specific tests were to include a capacity measurement and rate measurements at three temperatures (-29 °C, +24 °C, and +71 °C), both with and without poison present. The poison agreed upon for these tests was carbon tetrachloride at a concentration of 1000 ppm. In addition to these tests, SRTC was also to evaluate DEB and polystyrene-coated DEB (PSC DEB) with regard to radiation and pressure effects because these capabilities did not exist at the LANL test facility. All of these tests were conducted as previously described for TRUGETTER.

In Figure 20 the amount of hydrogen absorbed by DEB and PSC DEB getters is plotted as a function of time. Note the impact of test conditions on the maximum amount of hydrogen removed in each test. Previous experience with DEB at SRTC indicated that it was possible to overheat the DEB when rapidly exposing the sample to an excess of hydrogen, resulting in loss of reactivity. In an attempt to avoid this, several attempts were made to control the rate of hydrogen addition to the sample by slowly leaking it into the sample container. However, maximum hydrogen absorption for both DEB and PSC DEB was obtained by heating the sample container to approximately 50 to 60 °C as the reaction progressed to hasten completion. For example, in Figure 20, the amount of hydrogen absorbed by DEB (light blue curve and purple curve) increased rapidly from just over 8 mol kg^{-1} to over 10 mol kg^{-1} when heated to approximately
60 °C. The capacity data are summarized in Table 16. The values deemed most reliable are in bold format.

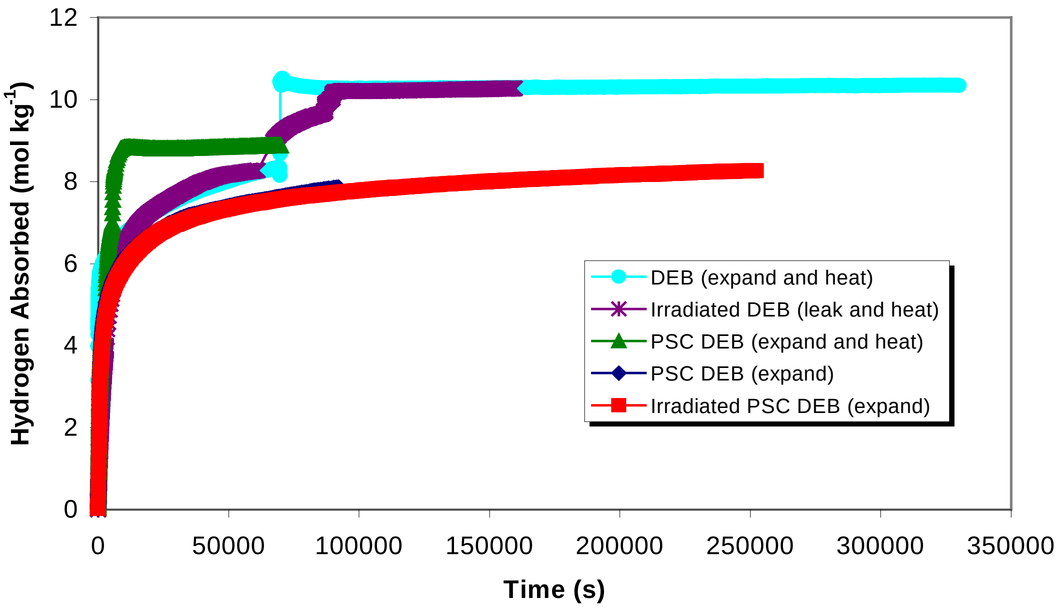


Figure 20. Capacity measurements for DEB samples.

Table 16. Summary of capacity data for DEB samples.

Sample Description	Hydrogen Capacity (mol kg^{-1})			
	Unirradiated	Method of H2 Addition	Irradiated	Method of H2 Addition
Uncoated DEB	**10.34**	Expand and heat	**10.28**	Leak and heat
	9.67	Leak without heat		
PS-Coated	**8.88**	Expand and heat	---	---
	7.86	expand without heat*	**8.27**	expand without heat*
	7.82	leak without heat	---	---

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

Figures 21, 22, and 23 show the effects of temperature and poison on rate of hydrogen removal at 50 % loading from vacuum, nitrogen and air for DEB and PSC DEB. The samples were loaded to 50 % based on the measured values in bold from Table 16 for the unirradiated samples.

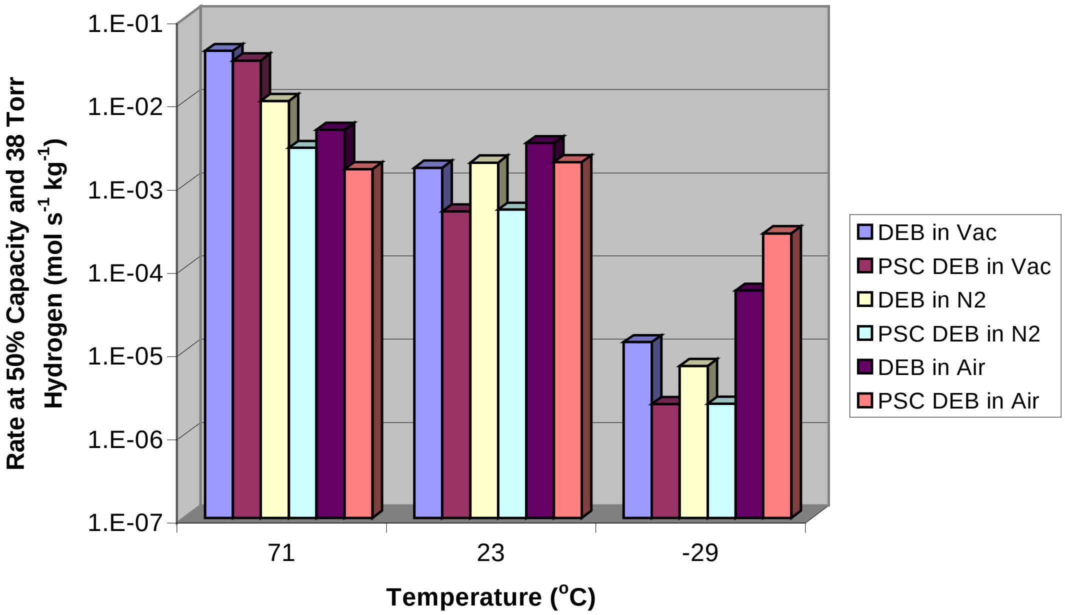


Figure 21. Effect of temperature on DEB and PSC DEB.

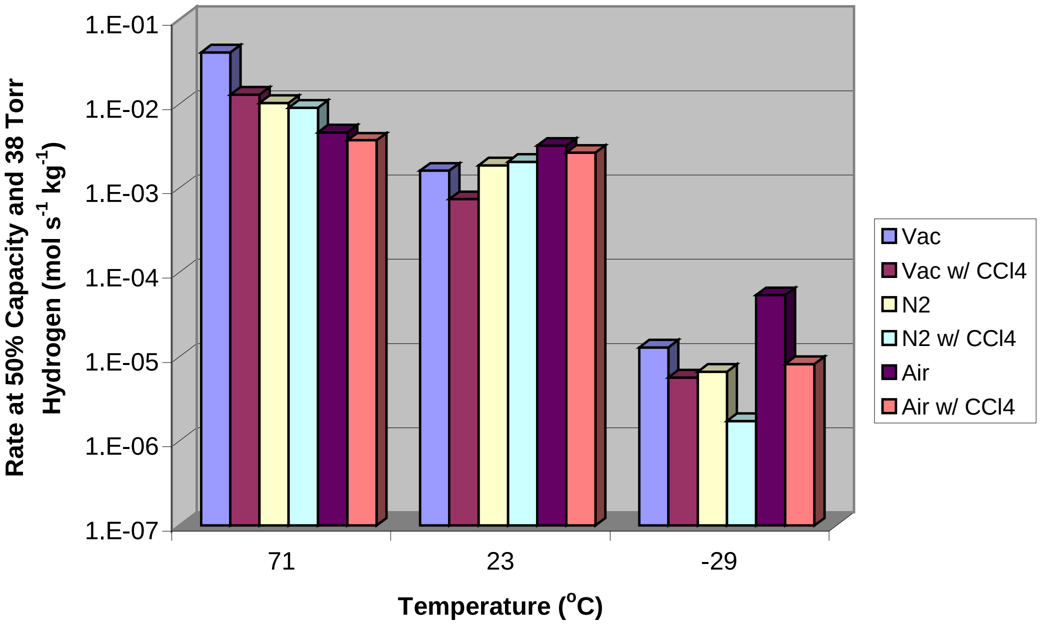


Figure 22. Effect of CCl4 on DEB.

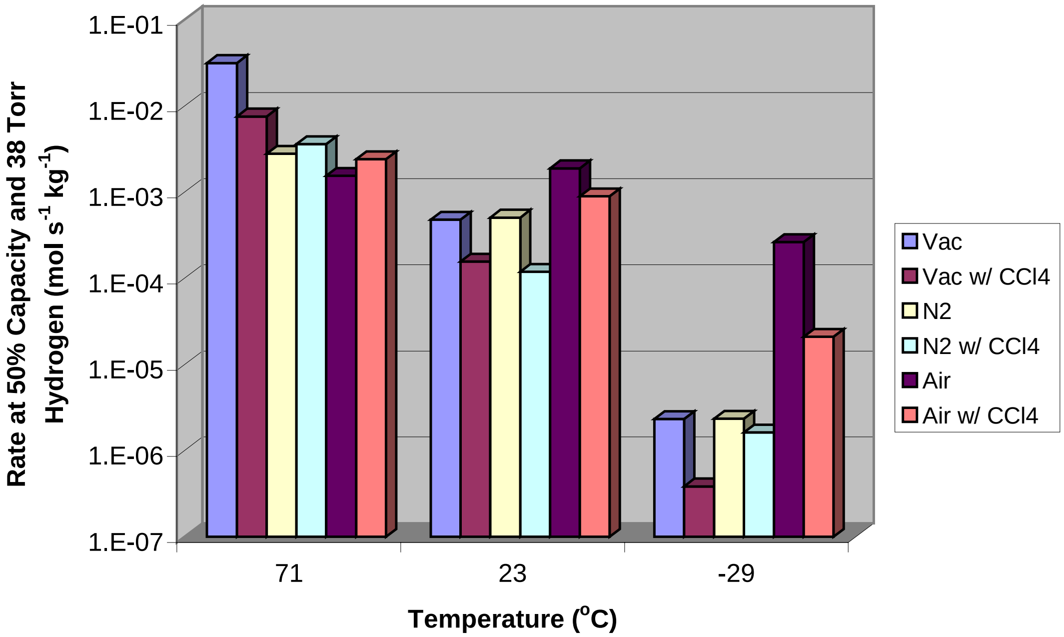


Figure 23. Effect of CCl4 on PSC DEB.

Poison screening tests were also run at ambient temperature with PSC DEB in the large-scale apparatus in the same manner as the tests run with TRUGETTER, except zeolite was not co-deployed with the getter. These tests were run to evaluate the effects of a large excess of poison (CCl4 and CO) on the hydrogen absorption characteristics of PSC DEB. Figure 23 depicts the results of these tests. The large excess of poison used in these tests (~ 50X the volume to mass ratio for the getter deployed in the TRUPACT-II) clearly has an impact on the rate of hydrogen absorption by PSC DEB. The rates at 50 % loading and 5 % hydrogen (38 Torr) for the control, 1000 ppm CCl_4, and 1000 ppm CO were 4.93E-04, 5.13E-05, and 2.42E-05 mol s^{-1} kg^{-1}, respectively.

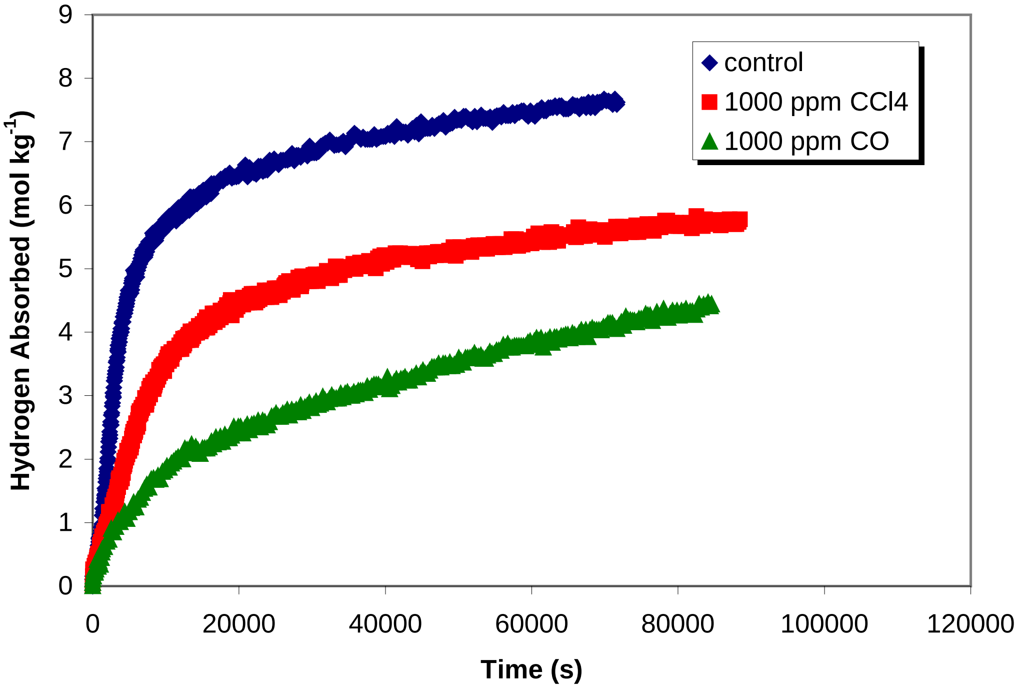


Figure 24. Effect of poisons on hydrogen absorption in nitrogen for PSC DEB in large-scale test vessel.

Table 17 summarizes the all of the rate data for the tests run in the small-scale vessels, including pressure and radiation effects.

Table 17. Rate data for DEB and PSC DEB in small-scale test vessel.

Atmosphere	Temperature (^oC)	Rate ($mol\ s^{-1}\ kg^{-1}$)			
		Control	Poison (1000 ppm CCl_4)	Pressure (50 psig)	Radiation (2.5E+04 Rad)
		Uncoated DEB			
Vacuum	71	4.07E-02	1.28E-02	N/A	N/A
	23	1.62E-03	7.43E-04	N/A	2.37E-03
	-29	1.29E-05	5.71E-06	N/A	N/A
Nitrogen	71	1.03E-02	8.97E-03	N/A	N/A
	23	1.86E-03	2.05E-03	1.55E-03	3.48E-03
	-29	6.68E-06	1.72E-06	N/A	N/A
Air	71	4.59E-03	3.69E-03	N/A	N/A
	23	3.19E-03	2.63E-03	4.94E-03	4.87E-03
	-29	5.38E-05	8.19E-06	N/A	N/A
		Polystyrene-coated DEB			
Vacuum	71	3.14E-02	7.56E-03	N/A	N/A
	23	4.80E-04	1.56E-04	N/A	2.42E-04
	-29	2.33E-06	3.85E-07	N/A	N/A
Nitrogen	71	2.79E-03	3.60E-03	N/A	N/A
	23	5.04E-04	1.18E-04	2.99E-04	1.22E-03
	-29	2.35E-06	1.63E-06	N/A	N/A
Air	71	1.55E-03	2.40E-03	N/A	N/A
	23	1.89E-03	8.95E-04	9.02E-04	2.19E-03
	-29	2.63E-04	2.09E-05	N/A	N/A

Conclusions

Results of Phase 2 testing demonstrate that hydrogen getters remain a viable alternative to support payload expansion in the TRUPACT-II. This effort provides a firm basis for design of prototype getter assemblies and scaling of Phase 3 tests. The key observations include:

- Enhanced polymer getter materials have been developed. Extensive testing of the enhanced polymer getter has demonstrated these materials exceed the SOW requirements for application in the TRUPACT-II.
- Full-scale production of polymer getter pellets has been demonstrated. These pellets have minimal loss in hydrogen absorption capacity and rate relative to the powder form.
- The polymer getter pellets have a hydrogen capacity of 6.3 mol kg^{-1}; so as little as 20 kg will provide 2X the required hydrogen capacity.
- The rate of hydrogen removal at 5 % hydrogen, ambient temperature and 50 % getter loading is 1.2×10^{-3} mol s^{-1} kg^{-1}, or 2.4×10^{-2} mol s^{-1} for 20 kg. The hydrogen removal rate is proportional to the hydrogen partial pressure or molar concentration.
- Low temperature performance of earlier polymer getter materials has been addressed. Reducing the temperature to –20 °F reduces the rate at 5 % hydrogen and 50 % loading to 1.4×10^{-5} mol s^{-1} kg^{-1}. Based on initial results, 20 kg should maintain the hydrogen concentration in the ICV at less than 0.4 %.
- Codeployment of the getter with zeolite and Hopcalite® catalyst has been demonstrated to mitigate the effects of all getter poisons evaluated (i.e., hexane, toluene, acetone, methanol, carbon tetrachloride and carbon monoxide).
- The gettering reaction is not reversible under transport conditions.
- Increasing the total pressure to 50 psig has minimal impact on absorption rate.
- Exposure to 2.5 x 104 rad gamma radiation has minimal impact on hydrogen absorption rate and capacity.

ATTACHMENT 1

Attachment 1
Polymer Hydrogen Getters

Hydrogen accumulation is a general problem for sealed containers. Hydrogen generated by chemical, electrochemical or radiolytic means accumulates becoming a flammability, or if sufficient oxygen is present, an explosion hazard. Hydrogen may also cause problems because of its chemical reactivity, its ability to embrittle metals, its thermal insulating ability (heat pipes), or its thermal conductivity (vacuum systems). In most application, venting the hydrogen adequately removes the hazard. When venting is not feasible, the hydrogen must be scavenged or gettered.

The general public seldom appreciates the widespread distribution of hydrogen hazards. The deformed AA or AAA batteries in a television remote control are bulged by internal hydrogen pressure. Sudden failure of the crimp seal on an alkaline cell can create an explosive atmosphere within in the confines of a device. Exchange of the hydrogen with the surrounding atmosphere quickly brings the hydrogen concentration below dangerous levels. Waterproof, batteries or battery-powered devices such as flashlights, cameras, SCUBA/marine equipment, vibrators, and equipment for inclement weather are more dangerous because they build up hydrogen and are prone to hydrogen/oxygen explosions. The explosions are typically initiated by a spark caused when turning the device on/off and can cause grave bodily injury. Almost all of these devices use a getter or recombiner to mitigate the hazard. Today, millions of units per year use the Sandia polymer getter/recombiner to effectively mitigate these hazards.

Sealed spars and structural frame members in items ranging from nuclear aircraft carriers to farm plows are subject to dangerous hydrogen accumulation. [Ref. NIOSH Report 473.] Venting is often impractical because it leads to undesired accumulation of substances within the hollow member. Vacuum insulation and heat transfer media are fouled by hydrogen because of its high thermal conductivity. Polymer hydrogen getters are effective at keeping hydrogen below conductive levels (<1 ppm) for years in vacuum or steam atmospheres. Many specific hydrogen getter systems have been developed, commercialized and deployed for the above and other devices. The polymer hydrogen getters are an enabling technology that allows the safe use of otherwise dangerous or ineffective devices. Getters typically represent less than 1% of the mass and cost of an item, yet their use allows safe operation.

Similar to consumer and industrial products, hydrogen gas in sealed radioactive material packages may reach levels and pressures that prohibit transportation and that are a serious safety concern. Per Nuclear Regulatory Commission requirements (e.g., 10CFR71.43(d), 10CFR71.65, and NUREG/CR 6673), the maximum amount of hydrogen allowable in the innermost confinement layer within a package is 5%. This impacts site closures (e.g., RFETS) and site transportation schedules (e.g., WIPP, SRS) since some wastes may exceed the 5% hydrogen limit.

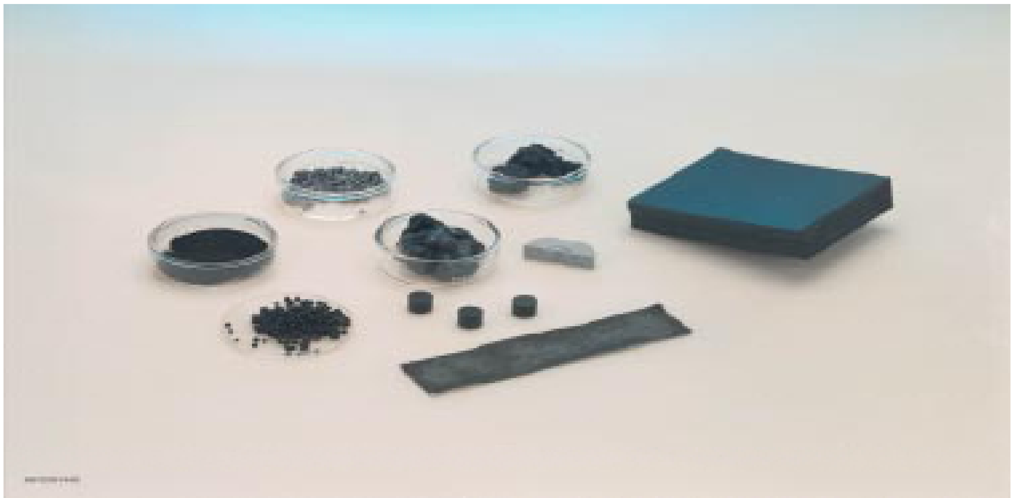
Commercially available polymer getters are in price range of $200-$2700/kg depending on type and quantity. Polymer-based getters are available in powders, pellets, and monoliths. The quantity of getter required for a specific package depends upon many factors. Operational temperature, hydrogen generation rate, internal volume of the package, other gases present, pressure, radiation exposure, and desired hydrogen concentration limits.

The polymer getters can be recycled to retrieve their precious metal content. The precious metals within the polymer getters may be available from the DOE strategic pool. If precious metals from the DOE pool are used, the cost of the getters would be reduced.

No special equipment or facilities are required to implement the use of polymer getters. The polymer getters can be manufactured and packaged in a form suitable for direct insertion into a package. The polymer getters have no known ES&H issues – they are chemically benign and passive in nature. (A Material Safety Data Sheet for polymer getters is included in Attachments 4 and 5.) They provide a considerable margin of safety to transport packages and their use should be of no significant concern to stakeholders. Users of the polymer getters (i.e., DOE Sites) should have neither operational difficulties nor objections to their application.

1. Commercial shipment of getter (>$100,000; 3-4 million units) for use in consumer products as manufactured by our licensee Vacuum Energy Inc.

2. Various forms of commercial hydrogen getters produced by Sandia National Laboratories.



ATTACHMENT 2

Table 2. TMFA Consolidated Phase 2 Test Plan Matrix.

EVALUATION CRITERION	TEMP. (°F)	PRESSURE	ATMOSPHERE	POISON	SITE	COMMENTS
CAPACITY [mol/kg]	+77 ≥ T < +160	Ambient	N_2 or vacuum	None	LANL SRTC SNL	SRTC shall also test DEB getter.
TEMPERATURE RANGE [mol H_2/s/kg @50% capacity ≡ "rate"]	–20, +23, +77 and +160	Ambient	$N_2 + H_2$ Air + H_2	Yes, all @ +77 °F; CCl_4 @ +77 °F, +160 °F	LANL SRTC	A sample of each getter to be aged 60 days @ +160 °F, rate and capacity measured in $N_2 + H_2$ or vacuum + H_2
POISONS [mol H_2/s/kg @50% capacity]	+77	Ambient	$N_2 + H_2$ Air + H_2	Yes	LANL SRTC	POISON tests incorporated in TEMPERATURE RANGE test series
PRESSURE [mol H_2/s/kg @50% capacity]	+77	50 psig	$N_2 + H_2$ Air + H_2	None	SRTC	
FREE LIQUIDS [calculation]	NA	NA	NA	NA	INEEL LANL SNL SRTC	Calculation: volume of H_2O produced by reaction of 62 mol of H_2
REVERSIBILITY	NA	NA	NA	NA	LANL SRTC	Load getter to full capacity; heat @ +160 °F; measure desorbed H_2
RADIATION [mol/kg; mol H_2/s/kg @50% capacity]	+77	Ambient	$N_2 + H_2$ or vacuum + H_2	None	SRTC	Getters to be exposed to γ-radiation at SRTC; SRTC to test DEB getter in addition to polymer-based getters
TEMPERATURE EFFECT [calculation]	NA	NA	NA	NA	INEEL LANL SNL SRTC	Calculation: heat of reaction of recombination of 62 mol of H_2
STRUCTURE / SHAPE	NA	NA	NA	NA	NA	tbd; tests to be performed on candidate STRUCTURE/ SHAPE
COMPATIBILITY	NA	NA	NA	NA	NA	All getters known to be compatible with TRUPACT-II and contents per MSDS; requires documentation
COST	NA	NA	NA	NA	NA	tbd
PASSIVE	NA	NA	NA	NA	NA	All getters passive; requires documentation.

Notes:
Each candidate getter to be evaluated. INEEL/LANL “DEB” getters; SNL/SRTC “polymer-based” getters.
Poisons: acetone, toluene, methanol, hexane, CO, CCl_4 @ 1000 ppm (others tbd; all TEMPERATURE RANGE / POISON tests with single poison).
Each test site shall employ and describe existing test method; LANL “dynamic” testing; SNL/SRTC “static” testing.
Measure of “rate” defined as: mol H_2/s/kg @50% capacity of getter.
Evaluation Criteria from: [TMFA] Statement of Work, Hydrogen Gas Getters Evaluation Program, July 16, 1999.

ATTACHMENT 3

Attachment 3 - Experimental for Acceptance Testing

We perform identical acceptance testing on all getter samples. We determine what we call a 10 Torr rate and an experimental capacity for hydrogen uptake. These conditions do not represent TRUPACT-II conditions, but rather allow us to compare equivalently measure data among numerous samples.

The gas handling apparatus (Figure 1) has been used extensively by Sandia for evaluation of numerous getters. We have a high degree of confidence in the accuracy of the results obtained from this apparatus. However, since the stainless steel apparatus is opened to the air on a daily basis, high vacuum measurements are limited by our ability to degas the reactor of absorbed atmospheric species. As a practical matter, vacuum levels ≤ 0.01 Torr require that extra attention be paid to the degas cycle. We are unable to bake out the entire apparatus, so we typically operate with a few milliTorr of residual gas during long experiments with sealed volumes. The apparatus includes both a 1000 Torr and 10 Torr MKS pressure heads manufactured by Baratron. Data is acquired with a National Instruments PCI-6035E data acquisition card in a PowerMac G4 running LabView Version 6i. The digital resolution of the PCI-6035E is 16 bits. With the system logging a data point at least every 10 minutes, we have a uptake rate sensitivity of 2.9×10^{-9} std. cc s^{-1} for these experiments.

Testing was done on getters by placing a 0.50 gram sample into a test tube. A tissue was taped over the opening of the test tube to avoid powder dispersion. The getter samples were degassed at 100 °C for 2 hours 10 minutes. The first experiment done on each sample was to measure uptake rate. Volumes A, B, C (Figure 2) were filled with ≈ 20 Torr of hydrogen. The hydrogen was then expanded into volumes D, and E to expose the sample to hydrogen. Pressure changes were recorded by the computer. Hydrogen pumping rates were calculated from the pressure change data, and are average rates for the pressure drop from 10.0 to 9.8 Torr. Any remaining gas was pumped off. The second experiment on the sample was to measure the capacity of the getter. Volumes A, B, C (Figure 2) were filled with ≈ 970 Torr of hydrogen. The hydrogen was then expanded into volumes D, and E exposing to the sample to hydrogen. The reactor was heated to 75 °C for several hours. The reactor was then allowed to cool to room temperature before stopping the experiment. Hydrogen uptake was calculated from the pressure change of both experiments.

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

The MKS pressure heads from Baratron and their controllers are accurate to 0.08% and are calibrated annually. Should one of the calibrated heads be unavailable a non-calibrated head that has be checked against the calibrated head maybe used. Temperature measurements are made with a K type thermocouple and a model DP116-KC1-A-MDS meter manufactured by Omega with an maximum error of ±1.5 °C. 99.99999% pure hydrogen is produced with a Whatman hydrogen generator model 75-32.

Exact values of pumping rates can vary between experiments. Gas uptake rate is sensitive to pressure, temperature, other atmospheric constituents, hydraulic restrictions, physical placement of the getter, and degassing history. Pumping rates should only be compared when generated in the exact same apparatus or when the differences caused by changing apparatuses are quantified. We highly recommend testing uptake rates under conditions representative of the actual deployment.

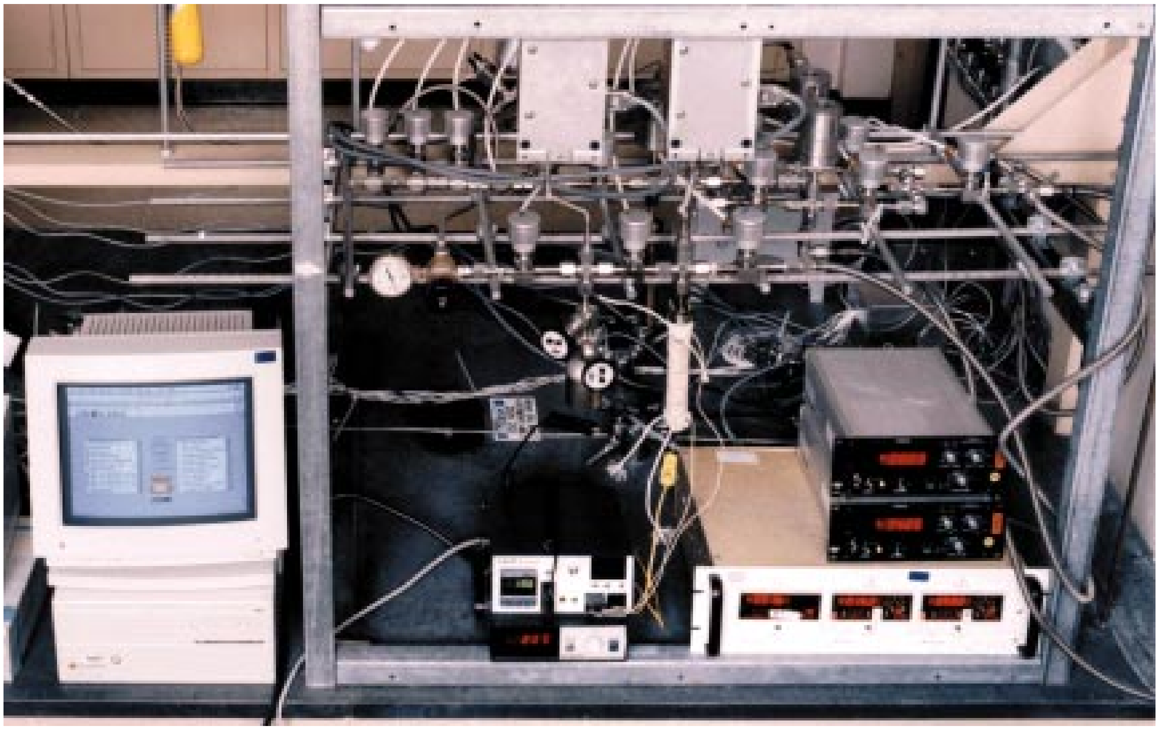


Figure 1. A photograph of the Sandia getter testing apparatus.

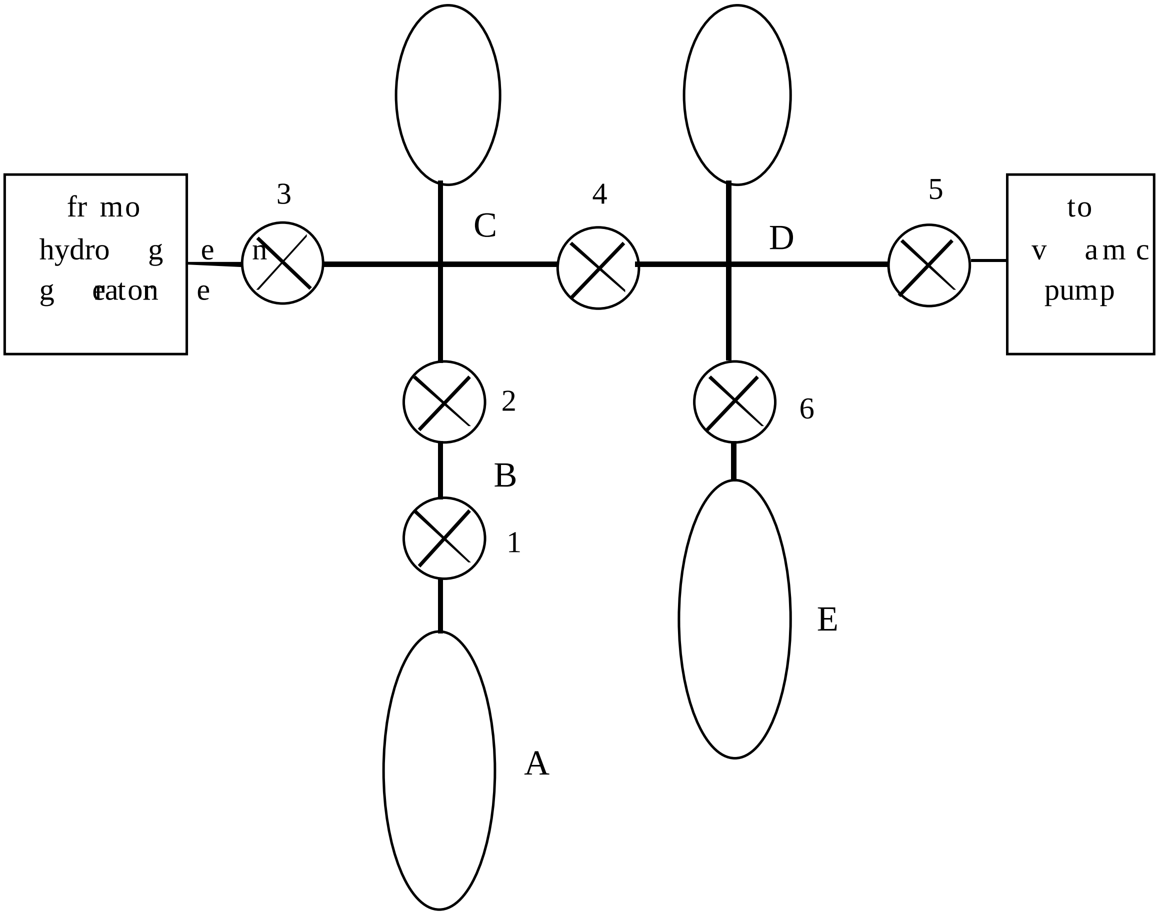


Figure 2. Schematic of apparatus. The volumes of the apparatus are as follows.

A	102.5 ml
B	3.9 ml
C	15.0 ml
D	17.1 ml
E	38.8 ml

Volume of sample and test tube is approximately 2.4 ml.

ATTACHMENT 4

MATERIAL SAFETY DATA SHEET

TRUGETTER Family of Hydrogen Absorbers

Manufacturer:	**Vacuum Energy, Inc.**
Address:	**13125 Shaker Square, D-201 Cleveland, Ohio 44120**
Telephone:	**(216) 991-7000**
Fax:	**(216) 991-7200**
Composition:	**Activated Carbon and/or Carbon Black Metals: Palladium and/or Platinum, Copper Organic Polymers (described below) Silicone Rubber This is a family of closely related formulations that provide the same function of scavenging hydrogen. They are available in various physical forms powders, pellets, coatings, etc. The data in this document applies to all of the formulations of TRUGETTER**
Trade Name:	**TRUGETTER**
Date:	**August 15, 2001**
General Safety/Handling:	**Materials are not dangerous. Can be stored and handled safely in air. Materials can absorb water and other active gases from the air which can later desorb under vacuum. Carbon in the materials can sorb vapors such as organic solvents, and should therefore be stored in an airtight impermeable container indoors, away from chemical storage compartments in a dry, inert gas atmosphere such as nitrogen or argon. Avoid conditions that can generate excessive dust.**

****

SECTION 1 - INGREDIENT INFORMATION

****

Chemical Name:

	CAS Numbe	Concentration
Activated Carbon and/or Carbon Black	**CAS #: 7440-44-0**	**30-90%**
Copper	**CAS #: 7440-50-8**	**0.1-5%**
Isobutylene-butene copolymer	**CAS #: 9003-29-6**	**1-10%**
Magnesium Carbonate	**CAS #: 546-93-0**	**1-5%**
Magnesium Hydroxide	**CAS #: 1309-42-8**	**1-10%**
Palladium	**CAS #: 7440-05-3**	**0.1-5%**
Platinum	**CAS #: 7440-06-4**	**0.1-5%**
Polymeric Rubbers (silicone, polybutene, polybutadiene, polybutadiene-*co*-styrene, trade secret)	**CAS #: 9003-28-5 CAS #: 9003-17-2**	**25-55%**
Poly 1,2-dihydro-2,2,4-trimethylquinoline	**CAS #: 26780-96-1**	**<2%**
1,3,5-Trimethyl-2,4,6-Tris (3,5-Di-Tert Butyl-4-Hydroxybenzyl) Benzene	**CAS #: 1709-70-2**	**<2%**

****

SECTION 2 - PHYSICAL/CHEMICAL CHARACTERISTICS

****

Boiling Point:	**N/A**
Specific Gravity (H_2O = 1):	**Ranges from 0.4 - 1.2**
Melting Point:	**N/A**
Vapor Pressure (mm Hg):	**Less than 1 Torr**
Solubility in Water:	**Less than 1%**
Appearance:	**Black solid**
Odor:	**No Odor.**
Physical State:	**Solid**
Percent Volatiles:	**None.**

****

SECTION 3 - REACTIVITY DATA

****

Stability:	**Unstable -** **Stable - X** **Conditions to Avoid - Avoid prolonged temperatures above 250^{o}F**
Incompatibility (Materials to Avoid):	**Avoid contact with strong oxidizing agents**
Hazardous Decomposition or Byproducts:	**Combustion in insufficient oxygen can produce carbon monoxide**
Hazardous Polymerization:	**May Occur -** **Will Not Occur - X** **Conditions to Avoid -**

SECTION 4 - FIRE AND EXPLOSION HAZARD DATA

****

Flash Point:	**Solid combustible material. Flash Point >300^{o}F.**
NFPA Hazard Classification:	**Health: 0** **Reactivity: 0** **Flammable: 1**
Extinguishing Media:	**CO2, foam, water. If appropriate, isolate fire and allow it to burn out.**
Special Fire Fighting Procedures:	**Cool uninvolved drums with water from hose. Use standard procedures for combustible solids.**
Unusual Fire and Explosion Hazards:	**None.**

SECTION 5 - HEALTH HAZARD DATA

Chronic Toxicity: Not tested for mutagenicity in the Ames test. No other applicable information has been found

Acute Toxicity:

- **Oral:** No applicable data have been found
- **Eye:** Possible mild irritant
- **Skin:** Possible mild irritant
- **Absorption:** No applicable data have been found
- **Inhalation:** No applicable data have been found
Powders can form nuisance dusts

Signs and Symptoms of Overexposure:

- **Eye:** Possible mild irritation
- **Skin:** Possible mild irritation
- **Absorption:** None expected
- **Ingestion:** None expected
- **Inhalation:** Possible mild irritation

Emergency and First Aid Procedures: On contact with skin, practice proper hygiene. On contact with eyes, flush thoroughly with water for 15 minutes, seek medical attention. On contact with skin wash affected areas with soap and water. Seek medical attention if problems persist.

SECTION 6 - CONTROL MEASURES

Respiratory Protection: No special precautions for operations that use bulk solid material. If material is sprayed with solvents, use proper source ventilation hoods, and fullface respirator with high efficiency filter media. When handling powder avoid generating dust conditions, and use fullface respirator.

Ventilation: Local Exhaust.

Personal Protective Equipment: Gloves and safety glasses.

SECTION 7 - PRECAUTIONS FOR SAFE HANDLING AND USE

Steps to be Taken in Case Material Is Released or Spilled:	**Use gloves when cleaning up spill. Sweep up spilled material. Place spilled material in container for disposal.**
Waste Disposal Method:	**Trash.**
Precautions to be Taken In Handling and Storage:	**Avoid unnecessary skin contact. Use protective gloves when handling this material. Do not take internally. Be aware of safe handling procedures.**
Other Precautions:	**None.**

NOTE: The data contained in this Material Safety Data Sheet relates only to the specific materials designated herein and does not relate to their use in combination with any other materials or in any process. The information herein is based on technical data that Vacuum Energy, Inc. believes to be reliable. It is intended to be used by persons with technical skill. Prior to use, users shall conduct their own investigations to determine the suitability of the information for their particular purpose, and appropriate warnings and safe handling procedures should be provided to handlers and users. Any use of this data must be determined by the user to be in accordance with Federal, State and local laws and regulations. Since conditions of use and suitability are beyond Vacuum Energy, Inc.'s control, risks of use and suitability are therefore assumed by the user, and Vacuum Energy, Inc. expressly disclaims all warranties including warranties of the merchantability and fitness for a particular purpose, express or implied, in respect to the use or suitability of the materials.

ATTACHMENT 5

Material Safety Data Sheet

MSDS Code: TRUGETTER

TRUGETTER

Family of Hydrogen Absorbers Pellets

Revision date: 03/22/2002 **Date Printed:** 03/22/2002

NFPA Classification:		**HMIS Classification:**	
Health:	1	**Health:**	1 *
Flammability:	1	**Flammability:**	1
Instability:	0	**Reactivity:**	0
Special Hazards:		**Personal Protection:**	B

* Indicates possible chronic health effects.

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Chemical Name: Chemical Mixture

Product Use: Absorbent.

Supplier:

ENGELHARD CORPORATION
CHEMICAL CATALYSTS, PROCESS TECHNOLOGIES
101 WOOD AVENUE
ISELIN, NJ 08830-0770
1-800-336-8559 OR 1-800-321-2747

For Chemical Emergency Call CHEMTREC (24 hours):
1-800-424-9300 (US, Canada, Puerto Rico, Virgin Islands)
1-703-527-3887 (Outside Above Area)

2. COMPOSITION / INFORMATION ON INGREDIENTS

Ingredient	Weight in Product (%)	Notes
1,3,5-Trimethyl-2,4,6-Tris (3,5-Di-Tert Butyl-4-Hydroxybenzyl) Benzene 1709-70-2	< 2	None.
Carbon 7440-44-0	25-90	None.
Copper 7440-50-8	0-5	None.
Isobutylene-Butene Copolymer 9003-29-6	0.1-10	None.

Magnesium Carbonate 546-93-0	0.1-5	None.
Magnesium Hydroxide 1309-42-8	0.1-10	None.
Palladium 7440-05-3	0-5	None.
Platinum 7440-06-4	0-5	None.
Poly 1,2-Dihydro-2,2,4-Trimethylquinoline 26780-96-1	< 2	None.
Polymeric Rubbers	20-55	None.
Polysaccharide	1-4	None.
Silica	3-6	None.

3. HAZARDS IDENTIFICATION

Emergency Overview:

Color:	Black
Form:	Pellets
Odor:	Odorless
Flash Point, °C:	> 148

Most Important Hazards: Overexposure may cause liver and kidney damage, and blood disorders. May irritate eyes. May cause skin irritation. Inhalation may result in respiratory irritation. May cause an allergic skin reaction. Harmful if swallowed. May cause gastrointestinal irritation, headache, nausea, vomiting and diarrhea.

Potential Health Effects:

Inhalation: Exposure to dust particles generated from this material may cause irritation of the respiratory tract. May result in symptoms similar to those of the common cold. May result in coughing, wheezing and difficulty breathing.

Ingestion: Harmful if swallowed. May cause headache. May cause pain, nausea, vomiting and diarrhea.

Skin Contact: May cause skin irritation. May cause dermatitis. May cause an allergic skin reaction.

Eye Contact: May irritate eyes. May cause pain and tearing. May cause blurred vision.

Carcinogenicity:

Ingredient	Weight in Product (%)	NTP (Y/N)	IARC (See Notes)	OSHA (Y/N)	ACGIH (See Notes)

1,3,5-Trimethyl-2,4,6-Tris (3,5-Di-Tert Butyl-4-Hydroxybenzyl) Benzene 1709-70-2	< 2	N	N	N	N
Carbon 7440-44-0	25-90	N	N	N	N
Copper 7440-50-8	0-5	N	N	N	N
Isobutylene-Butene Copolymer 9003-29-6	0.1-10	N	N	N	N
Magnesium Carbonate 546-93-0	0.1-5	N	N	N	N
Magnesium Hydroxide 1309-42-8	0.1-10	N	N	N	N
Palladium 7440-05-3	0-5	N	N	N	N
Platinum 7440-06-4	0-5	N	N	N	N
Poly 1,2-Dihydro-2,2,4-Trimethylquinoline 26780-96-1	< 2	N	N	N	N
Polymeric Rubbers	20-55	N	N	N	N
Polysaccharide	1-4	N	N	N	N
Silica	3-6	N	N3	N	N

Notes:
IARC: Y1=Carcinogenic to humans; Y2A=Probably carcinogenic to humans; Y2B=Possibly carcinogenic to humans; N3=Not classifiable as to its carcinogenicity; N=Not studied or probably not carcinogenic.
ACGIH: A1=Confirmed human carcinogen; A2=Suspected human carcinogen; A3=Confirmed animal carcinogen; A4=Not classifiable as a human carcinogen; A5=Not suspected as a human carcinogen; N=Not studied.

Chronic Health Hazards: Prolonged or repeated exposure to dust may cause pulmonary problems. May cause liver and kidney damage. May affect the blood and blood system.

Aggravated Medical Conditions: Eye ailments. Dermal ailments. Pulmonary disorders. Blood disorders. Kidney disorders. Liver disorders.
Individuals with Wilson's Disease are at increased risk of Copper poisoning.

4. FIRST AID MEASURES

Inhalation: Move person to fresh air. Aid in breathing, if necessary, and get immediate medical attention.

Ingestion: If person is conscious and able to swallow, give large amounts of water to dilute. If vomiting occurs, keep head lower than hips to prevent aspiration. Get medical attention immediately.

Skin Contact:	Wash with soap and water. Get medical attention if irritation persists.
Eye Contact:	In case of contact, immediately flush eyes with plenty of water for at least 15 minutes and get medical attention if irritation persists.

5. FIRE FIGHTING MEASURES

Flash Point, °C:	> 148
Autoignition Temperature, °C:	Not Determined
Lower Explosive Limit, %:	Not Determined
Upper Explosive Limit, %:	Not Determined
Extinguishing Media:	Foam. Water. Dry chemical.
Fire Fighting Procedures:	Positive pressure, self-contained breathing apparatus. Wear full protective clothing.
Unusual Fire and Explosion Hazards:	Not a fire or explosion hazard.

6. ACCIDENTAL RELEASE MEASURES

Spill Procedures:	Contain spillage. Scoop up or vacuum into a container for reclamation or disposal. Avoid dusting.

7. HANDLING AND STORAGE

Store in a cool, dry location away from incompatible materials.
Keep container closed.
Avoid contact with heat, sparks, open flame and static discharge.
Wash thoroughly after handling.
Avoid generating or breathing dust.
Avoid contact with eyes, skin and clothing.
Avoid contact with moisture.
Use with adequate ventilation.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Ingredient	Weight in Product (%)	OSHA PEL:	ACGIH TLV:

1,3,5-Trimethyl-2,4,6-Tris (3,5-Di-Tert Butyl-4-Hydroxybenzyl) Benzene 1709-70-2	< 2	None Established	None Established
Carbon 7440-44-0	25-90	None Established	None Established
Copper 7440-50-8	0-5	0.1 mg/m3 (Fume) 1 mg/m3 (Dust)	0.2 mg/m3 (Fume) 1 mg/m3 (Dust)
Isobutylene-Butene Copolymer 9003-29-6	0.1-10	None Established	None Established
Magnesium Carbonate 546-93-0	0.1-5	None Established	None Established
Magnesium Hydroxide 1309-42-8	0.1-10	None Established	None Established
Palladium 7440-05-3	0-5	None Established	None Established
Platinum 7440-06-4	0-5	1 mg/m3	1 mg/m3
Poly 1,2-Dihydro-2,2,4-Trimethylquinoline 26780-96-1	< 2	None Established	None Established
Polymeric Rubbers	20-55	None Established	None Established
Polysaccharide	1-4	None Established	None Established
Silica	3-6	20 mppcf or 80 mg/m3 ÷ %SiO2 (1993 Final Rule)	None Established

Unless otherwise noted, all values are reported as 8-hour Time-Weighted Averages (TWAs) and total dust (particulates only). All ACGIH TLVs refer to the 2000 standards. Unless otherwise noted, all OSHA PELs refer to 29 CFR Part 1910 Air Contaminants: Final Rule, January 19, 1989.

Personal Protective Equipment: Safety glasses with side shields. Wear suitable gloves.

Respiratory Protection: Use a NIOSH/MSHA approved respirator as necessary to protect from: dust. If respiratory protection is used, follow all requirements for respiratory programs set forth in OSHA regulations (29 CFR 1910.134).

Ventilation: General ventilation. Local exhaust ventilation as necessary to control dust, mist, vapor or fumes.

9. PHYSICAL AND CHEMICAL PROPERTIES

Form:	Pellets
Color:	Black
Odor:	Odorless

Vapor Pressure:	< 1torr	
Specific Gravity:	0.63g/cc	at 25 °C
Solubility (in water):	< 1%	

10. STABILITY AND REACTIVITY

Stability Data:	Stable
Conditions/Hazards to Avoid:	Temperatures above 120 °C. Moisture.
Incompatibility (Materials to Avoid):	Acids. Alkalies. Oxidizing agents. Reducing agents.
Hazardous Decomposition Products:	Oxides of carbon. Oxides of nitrogen.
Polymerization:	None anticipated.
Polymerization - Avoid:	None anticipated.

11. TOXICOLOGICAL INFORMATION

Information on Product:

No data available.

Information on Components:

Ingredient	Weight in Product (%)	Acute Toxicity - Oral	Acute Toxicity - Inhalation	Acute Toxicity - Dermal	Acute Toxicity - Other
1,3,5-Trimethyl-2,4,6-Tris (3,5-Di-Tert Butyl-4-Hydroxybenzyl) Benzene 1709-70-2	< 2	1,500 mg/kg (rat)	Not Available	Not Available	Not Available
Carbon 7440-44-0	25-90	Not Available	Not Available	Not Available	440 mg/kg intravenous (mouse)
Copper 7440-50-8	0-5	Not Available	Not Available	Not Available	3.5 mg/kg intraperitoneal (mouse)
Isobutylene-Butene Copolymer 9003-29-6	0.1-10	Not Available	Not Available	Not Available	Not Available
Magnesium Carbonate 546-93-0	0.1-5	Not Available	Not Available	Not Available	Not Available
Magnesium Hydroxide 1309-42-8	0.1-10	8,500 mg/kg (rat)	Not Available	Not Available	Not Available
Palladium 7440-05-3	0-5	Not Available	Not Available	Not Available	Not Available
Platinum 7440-06-4	0-5	Not Available	Not Available	Not Available	Not Available
Poly 1,2-Dihydro-2,2,4-Trimethylquinoline 26780-96-1	< 2	Not Available	Not Available	Not Available	Not Available

Polymeric Rubbers	20-55	Not Available	Not Available	Not Available	Not Available
Polysaccharide	1-4	7,060 mg/kg (rat)	Not Available	Not Available	Not Available
Silica	3-6	Not Available	Not Available	Not Available	Not Available

12. ECOLOGICAL INFORMATION

Information on Product:

Environmental Fate:	No data available.
Ecotoxicological Information:	No data available.

13. DISPOSAL CONSIDERATIONS

US EPA Waste Number: Not Regulated

Disposal of Waste Method: Local disposal laws and regulations will determine the proper waste disposal/recycling/reclamation procedure. Disposal requirements are dependent on the hazard classification and will vary by location and the type of disposal selected. All waste materials should be reviewed to determine the applicable hazards (testing may be necessary).

14. TRANSPORT INFORMATION

International Transport Regulations:

UN/PIN Number: Not Regulated

US Transportation Regulations:

DOT Classification: Not Regulated

Canadian Transportation of Dangerous Goods (TDG):

TDG Classification: Not Regulated

15. REGULATORY INFORMATION

International Inventories:

United States:	This product or its ingredients are listed on or compliant with the TSCA Inventory.
Canada:	This product or its ingredients are listed on or compliant with the DSL.
Europe:	Not Determined
Japan:	Not Determined
Australia:	Not Determined
Korea:	Not Determined

US Federal Regulations:

Ingredient	**Weight in Product (%)**	**Subject to SARA 313 Reporting**
1,3,5-Trimethyl-2,4,6-Tris (3,5-Di-Tert Butyl-4-Hydroxybenzyl) Benzene 1709-70-2	< 2	No
Carbon 7440-44-0	25-90	No
Copper 7440-50-8	0-5	Yes
Isobutylene-Butene Copolymer 9003-29-6	0.1-10	No
Magnesium Carbonate 546-93-0	0.1-5	No
Magnesium Hydroxide 1309-42-8	0.1-10	No
Palladium 7440-05-3	0-5	No
Platinum 7440-06-4	0-5	No
Poly 1,2-Dihydro-2,2,4-Trimethylquinoline 26780-96-1	< 2	No
Polymeric Rubbers	20-55	No
Polysaccharide	1-4	No
Silica	3-6	No

SARA 311/ 312 Hazard Categories:
Acute Health Hazard Chronic Health Hazard

CAA 602 Ozone Depleting Substances (ODS):
This product neither contains nor is manufactured with an ozone depleting substance subject to the labeling requirements of the Clean Air Act Amendments 1990 and 40 CFR Part 82.

VOC Content: None

US State Regulations:

VOC Content (CARB): Not Determined

Canadian Regulations:
WHMIS Classification:
Class D Division 2 Subdivision B
This product has been classified in accordance with the hazard criteria of the *Controlled Products Regulations* and the

MSDS contains all the information required by the *Controlled Products Regulations* .

16. OTHER INFORMATION

Revision number: 3

Section(s) Revised in this Version:
Product Name
Section 2: Composition/Information on Ingredients
Section 3: Hazards Identification
Section 9: Physical and Chemical Properties

Prepared By: Engelhard Corporate Environmental Health & Safety Group

The information in this Material Safety Data Sheet should be provided to all who will use, handle, store, transport, or otherwise be exposed to this product. This information has been prepared for the guidance of plant engineering, operations, management and for persons working with or handling this product. The information presented in the MSDS is premised upon proper handling and anticipated uses, and is for the material without chemical additions/alterations. We believe this information to be reliable and up-to-date as of the date of publication, but make no warranty that it is. Additionally, if this Material Safety Data Sheet is more than three years old, please contact the supplier at the phone number listed in Section 1 to make certain that this sheet is current. End of MSDS......

ATTACHMENT 6

date: March 20, 2002

to: Gracie Miranda, 8523 MS9281

from: Tim Shepodd, Noble Woo 8722 MS9403

subject: Flammabe Solid Test of TRUGETTER Pellets

A test was conducted on March 20, 2002 in building 916 room 120 to determine if the TRUGETTER materials should be classified as a flammable pellets. The presence of finely divided copper, palladium, and platinium requires that we determine if this formulated produce has the characteristics of its hazardous ingredients. The flammability tests performed on aforementioned subject were conducted in accordance with the United Nations, Transport of Dangerous Goods, Manual of Tests and Criteria.

The loose pellets were placed in an unbroken strip approximately 200 X 20 wide X 10 mm high on a glass surface. A lit butane torch was held to one end of the powder strip for two minutes. During this time, the pellets in direct contact with the flame began to glow orange and some ashes entrained in the gases from the torch flew away as orange glowing particles that rapidly extinguished. After the flame was removed, the pellets continued to smolder and glow. The smoldering did not advance and no flame propagated along the pellet. At the end of the five min test, the smolder front had proceeded zero distance from the end of the ignition zone. The material did not display the characteristics of a flammable solid.

On the following 3 pages are pictures taken during the test.

1. Before the test
2. During the 2 minute ignition period
3. After a total of 5 min

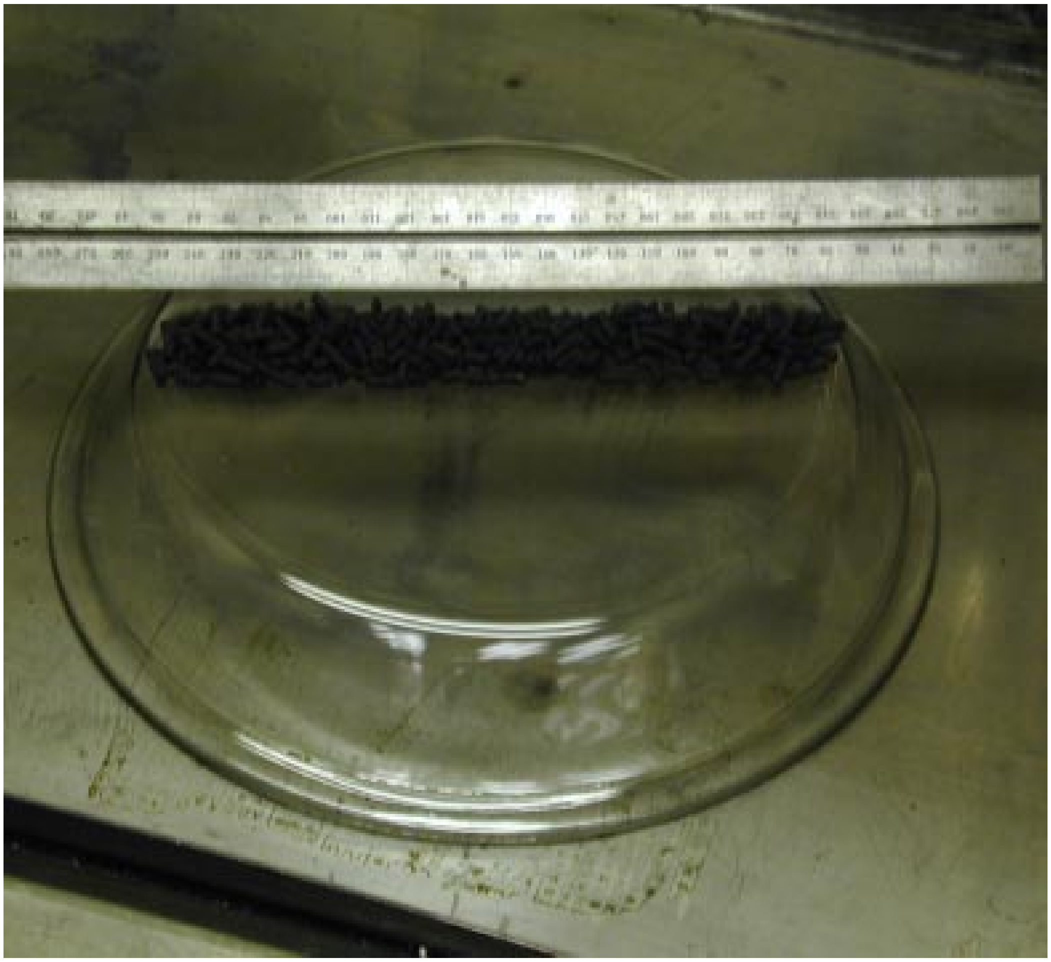


Photo #1: The pellet train before the ignition sequence.

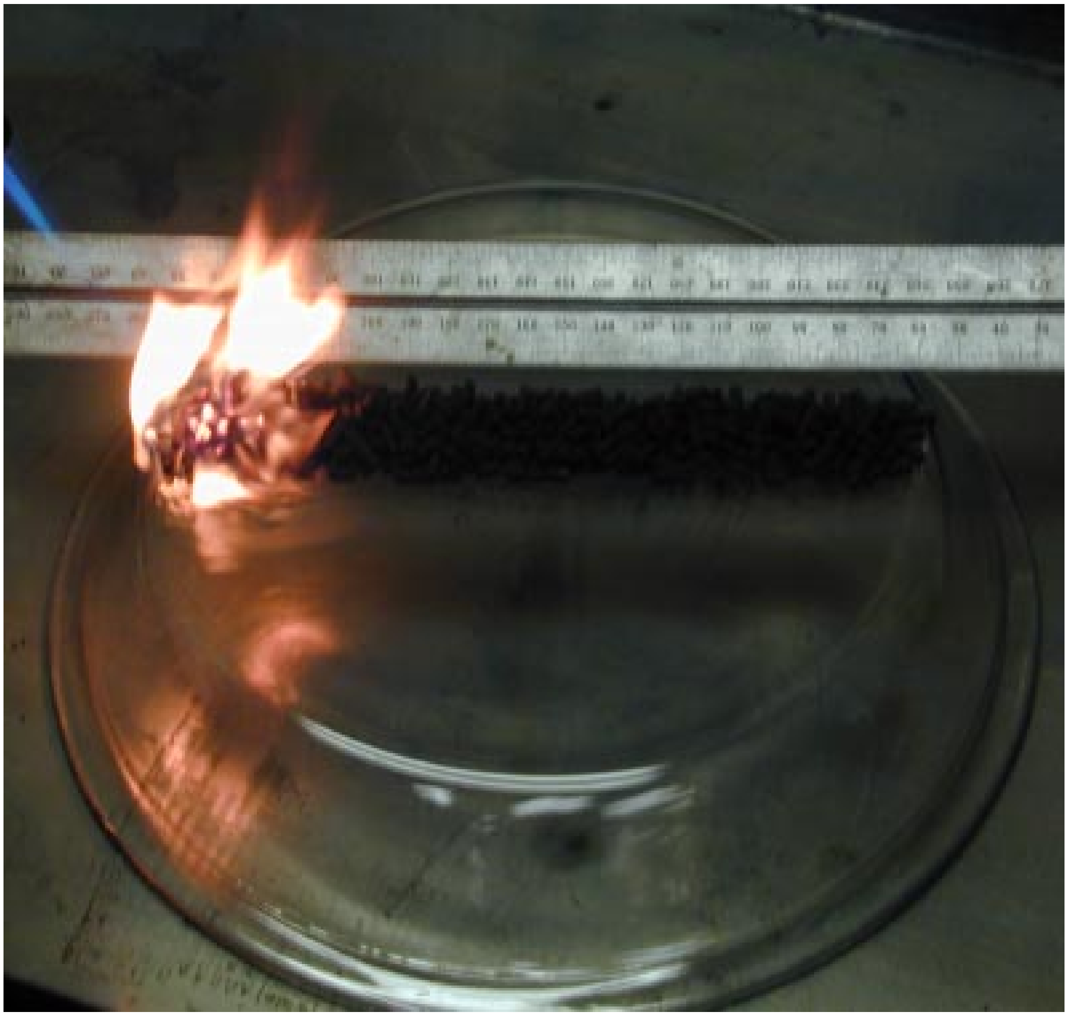
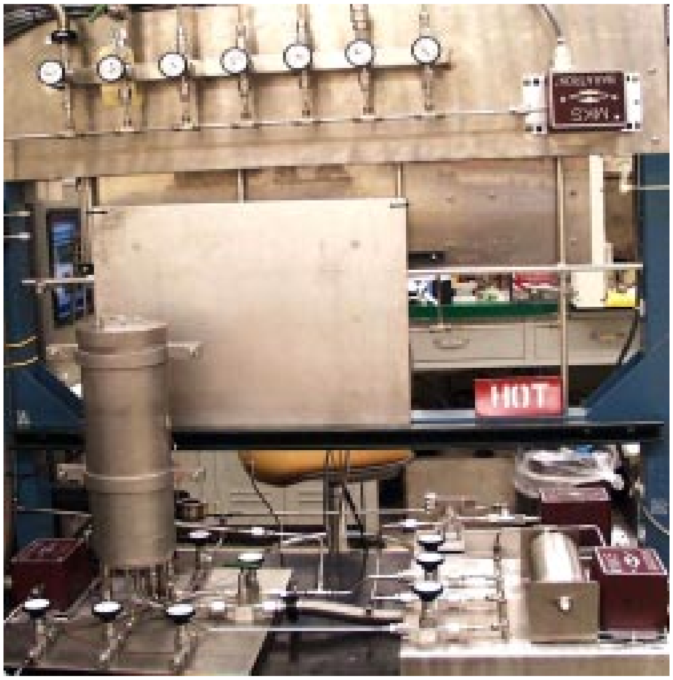


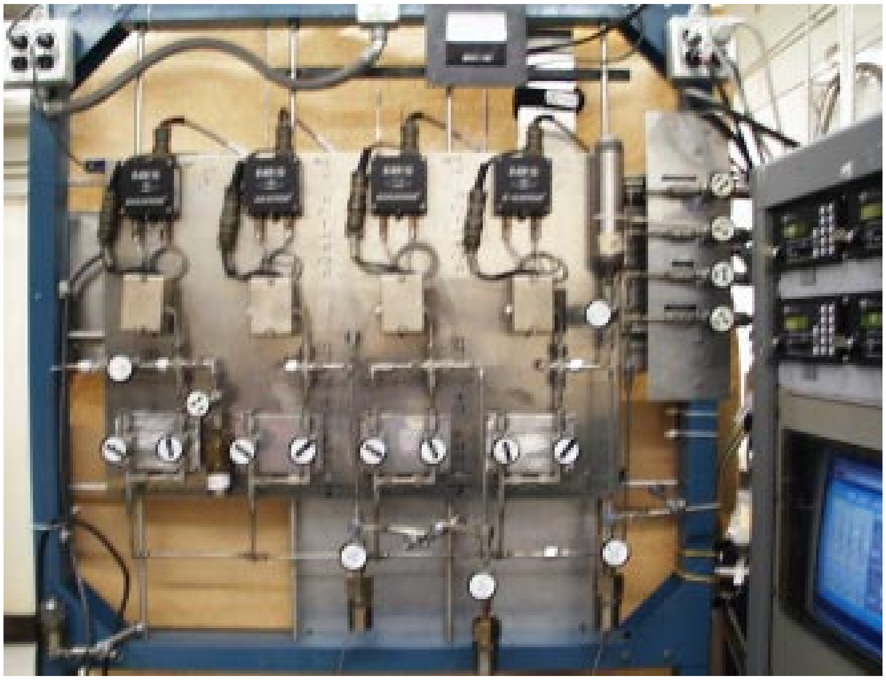
Photo #2: The pellet train during the 2 minute ignition sequence

Photo #3: The pellet train after 5 min from initiation. The smolder front (a wisp of smoke can be vaguely seen) has advanced no distance from the 3.5 cm ignition zone 3 min after removal of the ignition source.

ATTACHMENT 7


1
2
3
4


HOT

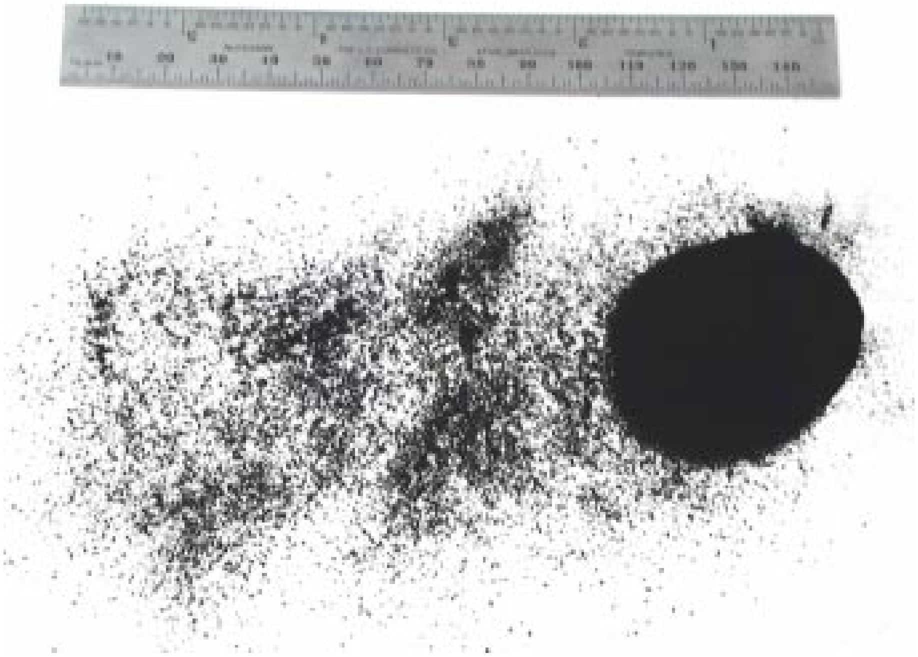



2


2
3


2


3



Distribution:

(9) Sharon Jones
Institute for Regulatory Science
5457 Twin Knolls Road, Suite 200
Columbia, Maryland 21045

INEEL
P. O. box 1625
Idaho Falls, ID 83415

1	Bob Curl
2	Whitney St. Michael
1	Eric Peterson, MS 2208

Westinghouse Savannah River Company
Savannah River Site
P. O. Box A
Aiken, SC 29801:

1	A. M. Murray, 773-A
1	A. F. Reichman, 773-41A
1	B. A. Daugherty, 705-3C
1	V. B. Bhambri, 705-3C
1	H. M Crapse, 703-A
1	R. R. Livingston, 773-A, Rm 160
10	J. M. Duffey, 773-A
1	J. D. Johnson, 773-A

Shaw E & I
5301 Central Avenue NE, Suite 700
Albuquerque, NM 87108

1	Jonathan Myers
2	Kevin Liekhus

John Kaszuba
Los Alamos National Laboratory
Chemistry Division, MS J514
Los Alamos, NM 87545

Sheila Lott
LANL – Carlsbad Operations

Mr. Brad Phillip
Vacuum Energy Inc.
13125 Shaker Square D-201
Cleveland, OH 44120

John Kaszuba
Los Alamos National Laboratory
P. O. Box 1663, MS J514
Los Alamos, NM 87545

SNL/CA:

10	MS M51/136	T. J. Shepodd, 8722
1	MS 9403	G. M Buffleben, 8722
1	MS 9403	W. R. Even, 8722
1	MS 9405	R. Stulen, 8700
1	MS 9403	W. Whinnery, 8722
3	MS 9018	Central Technical Files, 8945-1
1	MS 0899	Technical Library, 9616
1	MS 9021	Classification Office, 8511/Technical Library, MS 0899, 9616 DOE/OSTI via URL

SNL/NM

1	MS 716	Paul McConnell
1	MS 718	Ken Sorenson
1	MS 718	Marty Molecke
1	MS 779	Lawrence C. Sanchez
1	MS 701	Peter Davies

Murthy Devorakunda
Westinghouse TRU Solutions
6100 Seagull Ln., Suite 202
Albuquerque, NM 87109

115 North Main Street
Carlsbad, NM 88220

Department of Energy
P. O. Box 5400
Albuquerque, NM 87185
1 Steve Hamp, AL, SC-5
1 Ashok Kapoor, AL, SC-5
1 Gary Lanthrum, AL, 382-2
2 Ramoncita Massey, AL, 384-3
1 Pamela Saxman, AL, 384-3