DEVELOPMENT OF HYDROGEN GETTERS FOR USE IN TRANSURANIC WASTE SHIPMENTS

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ABSTRACT

Hydrogen gas generation is a key issue in the transportation of transuranic wastes in the TRUPACT-II shipping package. U.S. Nuclear Regulatory Commission regulations require that H_2 concentrations remain below the flammability limit of 5 percent by volume within all void volumes during a maximum 60-day shipping period. One of several approaches being pursued to meet this requirement for high gas generating wastes is the use of H_2 getters within the transportation package. Getters are substances that absorb H_2, thereby maintaining H_2 concentrations below the flammability limit.

The selected getter must be shown to be effective in credible scenarios expected under transportation conditions. The getter performance requirements include adequate H_2 absorption rate and capacity, ability to function over a temperature range of -20°F to +160°F and pressures up to 50 psig, and performance in the presence of radiation. In addition, it must be demonstrated that the getters will adequately perform in the presence of gases such as CO, hydrocarbon vapors (such as methanol and toluene) and chlorinated solvent vapors (such as carbon tetrachloride and trichloroethene). These gases, referred to as getter "poisons", may be present in some waste shipments, and are known to degrade the performance of some types of H_2 getters.

Several types of getters have been considered for use in TRUPACT-II containers. Metal hydride (ZrCo and $LaNi_4Al$ alloys) getters reversibly store H_2 within the alloy structure and the H_2 can be released upon heating so that the getters can be recycled. Organic polymers (DEB [1,4-bis(phenylethynyl)benzene] and a proprietary formulation developed by Sandia National Laboratories) contain double and triple carbon-carbon bonds that irreversibly hydrogenate upon exposure to H_2.

Operating in the presence of poisons is the most challenging requirement for these getters, and is the main thrust of the development and testing program. Required getter performance specifications are provided, along with an update on the status of the getter testing effort.

INTRODUCTION

The Transuranic Package Transporter-II (TRUPACT-II) packaging, certified by the U.S. Nuclear Regulatory Commission (NRC) as a Type B container, is designed for the shipment of contact-handled transuranic (CH-TRU) wastes from the U.S. Department of Energy (DOE) sites to the Waste Isolation Pilot Plant (WIPP). Since it was originally issued in 1989, the TRUPACT-II Certificate of Compliance [1] has been revised primarily to expand the allowable payload of the TRUPACT-II and allow shipment under less restrictive conditions. One of the restrictions on CH-TRU waste shipments is the 5 percent limit (by volume) on hydrogen concentrations imposed by the NRC.

Hydrogen gas generation and accumulation can result from the alpha radiolysis of hydrogenous waste and packaging materials coupled with certain waste packaging configurations. The combination of high activity wastes with multiple layers of packaging results in specific waste forms that do not meet transportation limits for hydrogen gas concentration. Waste types that have the potential for exceeding the hydrogen limit are the plutonium (Pu)-238 (heat source plutonium) wastes at Los Alamos National Laboratory (LANL) and Savannah River Site, and other high loaded wastes at other sites. Potential strategies for addressing gas generation limitations consist of the following three components.

- Demonstrate the Absence of Hydrogen (Less Than 5 Percent Hydrogen): This strategy would comply with the current limit of 5 percent hydrogen by implementing a bag breaching technology (to ensure the release of hydrogen from the inner confinement layers) in conjunction with the use of hydrogen gas getters (to scavenge the hydrogen released from the payload containers). Relief from the limits could also be achieved to a limited extent by using waste-specific characterization information to reduce the level of conservatism in the gas generation analysis.
- Demonstrate the Absence of Oxygen: This strategy would demonstrate safety by ensuring the absence of oxygen (by means of inerting, use of recombiners, bag breaching, or credit for naturally occurring recombination), without limiting the hydrogen. This option would challenge the current regulatory requirement of less than 5 percent hydrogen by using reasoned justifications and testing.
- Demonstrate No-Consequence of Potential Flammability Event: This strategy would ensure safety of shipment by demonstrating that the system is robust and safe under transportation conditions. This option would require the testing of a sealed system (e.g., ARROW-PAK™) and analysis to show that it will survive a potential flammability event. This option challenges the regulatory position on less than 5 percent hydrogen.

This paper describes the application of hydrogen getter materials in the TRUPACT-II. Approval of such a program by the NRC would be based on the results of a getter evaluation program, which is currently in progress. The objective of this evaluation program is not to develop new hydrogen gas getter materials, but to evaluate existing materials for their potential to address the performance requirements, and to develop a getter deployment methodology for the TRUPACT-II. Performance specifications that must be met for the use of getters in the shipping package are provided in the following section.

GETTER PERFORMANCE SPECIFICATIONS

Requirements that must be met for the use of getters in the TRUPACT-II shipping package are based on the general requirements of 10 CFR Part 71 [2]. These requirements include:

- Assume bounding credible scenarios for calculations and testing
- Identify the getter operational life and capacity
- Identify communication pathways between getter and hydrogen gas
- Effects of poison gases on getter performance
- Chemical compatibility of getters with the payload and packaging
- Generation of free liquids (water) from getter reactions
- Reversibility of getter reactions
- Effects of temperature on getter performance
- Effects of pressure (especially the minimum operating pressure) on getter performance.

The technical specifications resulting from these general requirements are:

<u>Potential Poisons</u>: The getter performance must be effective in the presence of other gases also known to be present in TRU waste. An extensive list of potential gases that potentially may be present in the total inventory of TRU waste drums is provided in the WIPP RCRA Part B Draft of Permit, Chapter C [3]. This list has been revised to only include potential gases and maximum concentrations that are specific to the TRU waste content codes that may require getters for transportation. The getter evaluation program has determining the threshold concentrations of representative gases that affect gettering rate and capacity.

<u>Compatibility</u>: The getter must be chemically compatible with the TRUPACT-II payload and construction materials. Specifically, the getter material must demonstrate that it is non-reactive

(except with H_2), non-pyrophoric, non-gas generating, and compatible with carbon steel, stainless steel, butyl o-rings, aluminum, and ABS plastic.

Operating Temperature Range: The payload for the TRUPACT-II, including the getter, must meet the "normal conditions of transport" as identified in 10 CFR 71 [2]. The minimum and maximum temperature conditions, under which the getter material must function, are –20°F and +160°F.

Pressure: The payload for the TRUPACT-II, including the getter, must meet the "normal conditions of transport" as identified in 10 CFR 71[2]. The pressure conditions identified in this regulation are zero to 50 psig.

Reversibility: Desorption of hydrogen from the getter during the shipping period is not acceptable, since it could potentially result in the hydrogen concentration exceeding the 5 percent limit.

Getter Rate and Capacity: The maximum expected hydrogen gas generation rate in a fully loaded TRUPACT-II container is 1.2×10^{-5} mole/sec for a maximum shipping period of 60 days. The getter must be capable of absorbing hydrogen at this rate or greater for the anticipated waste storage and shipping times.

Free Liquids: No generation of free liquids is acceptable under normal transport conditions. Up to 28 liters of free liquid may be acceptable under accident conditions.

Temperature Effect from Getter: Heating due to exothermic heat of reaction must be identified and evaluated with respect to it impact on getter performance. Heat of reaction should be quantified as Watts/mole H_2.

Passive Versus Active Getter Systems: Only passive (no external energy sources applied) systems are acceptable. This ensures that no potential ignition source is introduced into the TRUPACT-II.

Radiation Effects on Getter: Radiation effects on the getter performance must be understood. Since the getter will be located within the inner containment vessel (ICV) but outside of the drums, the energy deposition will be minimal.

Additional Engineering Requirements: Additional specifications related to the practical deployment of getters in the TRUPACT-II ICV have to be developed and defined. The volume of the getter material required to support shipping of the high activity waste must be determined based on the getter rate and capacity, assuming a maximum hydrogen gas generation rate of 1.2×10^{-5} mole/sec over a 60 day shipment period. The getter materials must be engineered into a form or package such that it can be deployed within the confines of the ICV, assuming a available ICV cavity volume loaded with 14 55-gallon drums of 2,450 liters. The structural integrity of the engineered form must also be determined to address any potential mechanical issues, and the optimal location(s) of the getter within the ICV should also be defined.

CURRENT STATUS

Various types of hydrogen getters have been extensively used in commercial and defense applications for the last twenty years. These applications include sealed vacuum devices, vacuum insulated panels, vacuum insulated oil well production piping, heat exchangers, nuclear weapons, and battery operated consumer products such as waterproof flashlights. Getters used in sealed vacuum devices can reliably maintain partial pressures of hydrogen as low as 0.05 torr (0.0001 atm) for extensive periods of time. The DOE getter evaluation program is focused on adapting these existing getters for use in TRUPACT-II containers.

Two general types of hydrogen getters exist: reversible and irreversible. Reversible getters are based on metals or metal alloys such as ZrCo, $Zr(FeV)_2$, and $LaNi_5$. The gettering behavior of these materials is temperature dependent. Hydrogen will be absorbed and stored within the metallic matrix as a hydride phase at lower temperatures, and can be released at higher temperatures. The surface of the getter is often coated with a noble metal such as platinum or palladium, to prevent oxidation and provide a catalytic surface for the decomposition of diatomic hydrogen to monoatomic hydrogen.

Irreversible getters include organic and inorganic compounds. Inorganic getters are based on oxides such as manganese dioxide (MnO_2). Hydrogen reacts with the oxide to yield a partially reduced oxide (manganese sesquioxide [Mn_2O_3]) plus water. A desiccant such as calcium oxide can be added to absorb water that is generated as a reaction product.

Organic hydrogen getters form a different class of irreversible getters. These getters are hydrocarbon compounds that contain double or triple carbon-carbon bonds that hydrogenate upon exposure to hydrogen by forming single carbon-carbon bonds. The most common organic hydrogen getter is DEB [1,4-bis(phenylethynyl)benzene], which was developed by the Allied-Signal Kansas City Plant. DEB is a nontoxic crystalline solid containing two triple carbon-carbon bonds. One mole of DEB reacts with four moles of H_2. The standard formulation for the DEB getter is a mixture of 75 percent DEB and 25 percent carbon catalyst containing 5 percent palladium. The getter reacts rapidly and irreversibly with hydrogen, with a capacity of

240 to 330 cm^3 hydrogen per gram. The reaction is nearly stoichiometric, and proceeds to greater than 90 percent of the theoretical capacity. DEB getter material blended with silicon and natural rubbers has been used to form seals and linings in weapons for several years.

Another irreversible organic hydrogen getter is a polymer-based system developed by Sandia National Laboratories (SNL). This material incorporates a polymer getter compound, activated carbon, and a noble metal catalyst, dispersed in a rubber matrix. This polymer getter has several advantages over DEB, and is replacing DEB in several commercial applications.

The key issue for the use of any of these getters for TRU waste transportation is adapting the getters for the TRUPACT-II environment. The environmental parameter of greatest concern is the potential presence of gases that may inactivate the getter or catalyst. Chlorinated solvent vapors can deactivate metal catalysts and free radical initiators such as sulfur dioxide and nitrogen dioxide can deactivate organic getter compounds. The compounds that affect getter performance are referred to as “poisons”.

It appears, based on studies done to date, that irreversible organic getters show the most promise for TRUPACT-II application. The DOE is pursuing two technologies in parallel to modify existing getter systems for use in TRU waste transportation systems. These approaches are summarized below.

1. One group of investigators at LANL and the Idaho National Engineering and Environmental Laboratory are testing DEB particles (5 to 500 microns) that are micro-encapsulated in a semi-permeable polymer coating that is selective for hydrogen.

2. A second group at Sandia/Livermore is working with the polymer-based system developed by SNL. The advantage of this material is that it incorporates a polymer getter compound, activated carbon, and a noble metal catalyst, dispersed in a rubber matrix. The material will absorb poisons, but they will preferentially remain within the rubber matrix so the active getter and catalyst remain protected.

The goal of these programs is to develop and certify a getter system that is specifically tailored for use in TRUPACT-II containers to allow the shipment of TRU waste payloads that would otherwise exceed the 5 percent hydrogen limit.

SUMMARY

The use of hydrogen gas getters is a potential solution to the shipment of Pu-238 and other high activity CH-TRU wastes, which are restricted by their gas generation potential. An effective getter material must be shown to function under expected transportation conditions with NRC approval based on a SAR revision. Two different materials are being investigated by the DOE for potential deployment.

REFERENCES

[1] U.S. Nuclear Regulatory Commission, 2001, Certificate of Compliance No. 9218, Revision 12. U.S. Nuclear Regulatory Commission, Washington, D.C.

[2] Title 10, Code of Federal Regulations, Part 71 (10 CFR 71), *Packaging and Transportation of Radioactive Material*, 1-1-98 Edition.

[3] Waste Isolation Pilot Plant Hazardous Waste Facility Permit NM4890139088-TSDF, New Mexico Environment Department, Santa Fe, New Mexico.