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TEST PLAN FOR HYDROGEN GETTERS PROJECT-PHASE II

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ACRONYMS AND ABBREVIATIONS

DEB	1,4-bis(phenylethynyl)benzene
DOE	U.S. Department of Energy
LANL	Los Alamos National Laboratory
MDP	Matrix Depletion Program
NIST	National Institute of Standards and Technology
NRC	U.S. Nuclear Regulatory Commission
RTV	room temperature-vulcanizing
TRU	transuranic
TRUPACT-II	Transuranic Package Transporter-II
TRUPACT-II SARP	*Safety Analysis Report for TRUPACT-II Shipping Package* (NRC 1996)
VOC	volatile organic compound
WIPP	Waste Isolation Pilot Plant

1.0 SUMMARY

Hydrogen levels in many transuranic (TRU) waste drums are above the compliance threshold, therefore deeming the drums non-shippable to the Waste Isolation Pilot Plant (WIPP). Hydrogen getters (alkynes and dialkynes) are known to react irreversibly with hydrogen in the presence of certain catalysts. The primary purpose of this investigation is to ascertain the effectiveness of a hydrogen getter in an environment that contains gaseous compounds commonly found in the headspace of drums containing TRU waste. It is not known whether the volatile organic compounds (VOCs) commonly found in the headspace of TRU waste drums will inhibit ("poison") the effectiveness of the hydrogen getter.

The results of this study will be used to assess the feasibility of a hydrogen-getter system, which is capable of removing hydrogen from the payload containers or the Transuranic Package Transporter-II (TRUPACT-II) inner containment vessel to increase the quantity of TRU waste that can be shipped to the WIPP.

Phase II for the Hydrogen Getters Project will focus on four primary objectives:

- Conduct measurements of the relative permeability of hydrogen and chlorinated VOCs through Tedlar (and possibly other candidate packaging materials)
- Test alternative getter systems as alternatives to semi-permeable packaging materials. Candidates include DEB/Pd/Al2O3 and DEB/Cu-Pd/C.
- Develop, test, and deploy kinetic optimization model
- Perform drum-scale test experiments to demonstrate getter effectiveness

2.0 BACKGROUND

2.1 Statement of Mixed Waste Treatment Need

Approximately 9,000 of the ~23,000 TRU waste drums at Los Alamos National Laboratory (LANL) are currently unshippable to the WIPP because they exceed the wattage (decay heat) limits, as specified in the TRUPACT-II SARP (NRC 1996). These limits are derived from worst-case calculations of the amount of hydrogen expected to be generated within the innermost bag by radiolysis during a 60-day shipping period.
Of the ~9,000 unshippable TRU drums at LANL, about 3,000 exceed wattage limits by less than a factor of 3. The Matrix Depletion Project (MDP) is expected to result in raising the wattage limits by a factor of about 3, in which case these drums would be deemed shippable.

About 3,000 drums exceed wattage limits by between 3 and 12 times. For these drums, the proposed plan is to open the drums, release the accumulated hydrogen through piercing of plastic bag confinement layers, and reclose the drums to meet wattage limits. This process will not generate additional drums for disposal.

The remaining ~3,000 drums, which exceed wattage limits by more than 12 times, would still exceed wattage limits even if inner layer elimination reduced the resistance to hydrogen transport. The drum contents would need to be divided amongst a number of drums to bring individual container wattage limits to acceptable levels. For the ~200 drums whose wattage limits are exceeded by >84 times, hundreds of drums would be needed to store the separated contents. This increase in drums would result in significantly greater handling costs and greater TRU waste volumes.

Treatment facilities, if and when they are built, would also be expensive options. One estimate shows that it would cost ~$1,300 per drum (U.S. Department of Energy [DOE] 1995) to treat TRU waste at a facility proposed for the Idaho National Engineering and Environmental Laboratory.

Hydrogen getters would be used to reduce the hydrogen levels in the drums whose wattage limits exceed 12 times. This would reduce the number of additional drums generated by repackaging by over 2,600 drums. For each drum, a cost of between $30 and $300 would be needed to introduce the getter to remove the gaseous hydrogen. Using a cost estimate of $10,000 per drum to treat, repackage, characterize, certify, transport, and emplace a drum of TRU waste at the WIPP, this technology can save the program over $23 million at LANL alone.

2.2 Technology Concept and Function

Hydrogen recombiners have been proposed as a solution to the problem of hydrogen build-up. Hydrogen recombiners are noble metal catalyst beds that remove hydrogen gas by reaction with oxygen to form water. However, the NRC rejected the use of recombiners for removing hydrogen from the TRUPACT II because of concerns about:
1) possible poisoning of the recombiner by other gases in the headspace.
2) recombiner performance under low oxygen, even anoxic, conditions.
3) recombiner performance in sub-freezing temperatures which would result in the formation of an ice coating on the active surface.

Hydrogen getters are solid materials that scavenge hydrogen from the gas phase and chemically and irreversibly binds it in the solid state. Hydrogen getters do not require the presence of oxygen to be effective. They do not produce water as a reaction product. They belong to a class of compounds called alkynes, which are characterized by the presence of carbon-carbon triple bonds. The triply-bonded carbon atoms in alkyne compounds will, in the presence of suitable catalysts such as palladium (Pd), irreversibly react with hydrogen to form the corresponding saturated alkane compounds.

Hydrogen getters of this class were originally developed for use in nuclear weapons by Sandia National Laboratory and the Kansas City Division of Allied-Signal. The getters were used to protect electronic components in sealed assemblies from hydrogen corrosion and are currently being used to provide secondary confinement for tritium shipping containers.

Many compounds and formulations have been tested (Sheppod et al. 1989; Smith and Sheppod 1990). The best performance has been achieved with 1,4-bis(phenylethynyl)benzene (DEB) (Figure 2-1). DEB is a nontoxic, nonmutagenic, crystalline solid. Because DEB is a dialkyne (containing two triple bonds), one mole of DEB reacts with 4 moles of hydrogen (2 moles react to form corresponding dialkene, an additional 2 moles react to form dialkane). DEB melts at 179°C, whereas the fully hydrogenated product melts at 87°C. The standard formulation for the DEB getter is a mixture of 75 percent DEB and 25 percent carbon catalyst (5 percent Pd on carbon). The production process is quite simple: the two materials are mixed together in a ceramic jar mill for several hours after which the DEB getter is ready for use. It has been shown to be stable in the absence of hydrogen for up to 18 months (at 70°C, under N_2).

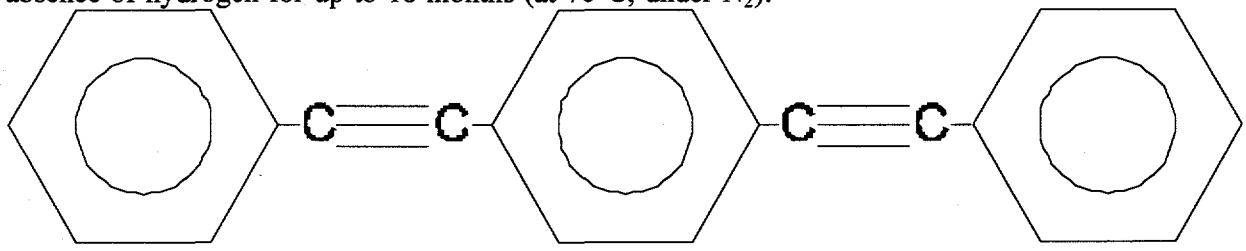

Figure 2-1. Structure of 1,4-bis(phenylethynyl)benzene

The DEB getter reacts rapidly, exothermically (~30 kcal/mole H_2), and irreversibly with hydrogen. It has a capacity of 240 to 330 cm^3 hydrogen per gram. The reaction is nearly stoichiometric and proceeds to >90 percent of the theoretical capacity. In experiments in a nitrogen atmosphere with a hydrogen addition rate of about 10^{-3} cm^3/sec, the hydrogen concentration was maintained at less than 5 ppm until the getter had reacted with >90 percent of its theoretical capacity. The reaction rate with hydrogen is temperature- dependent and proceeds more rapidly as the temperature is increased.

In the presence of oxygen, recombination reactions on the Pd catalyst will produce water in addition to hydrogenating the dialkyne. Thus, the material acts as both a getter and recombiner in the presence of air. The getters also have been found to be hygroscopic in air environments.

In FY98, experiments were performed at Los Alamos to investigate whether other compounds expected to be present in the headspace of TRU waste would affect the performance of the DEB getter. These test showed that DEB was unaffected by toluene, hexane, acetone and methanol. However, CO and several chlorinated VOCs (e.g. carbon tetrachloride, trichloroethylene, trichloroethane, chloroform and methylene chloride) did inhibit the reaction of H2 with DEB. It is clear that a solution to the poisoning problem must be found for DEB to maintain its effectiveness toward removal of H2 from TRU waste.

2.3 Current Status or State of Development

The DEB formulation has been successfully incorporated into several forms, including powder, pellets, shaped polyethylene composite, a urethane adhesive film, and a castable room temperature-vulcanizing (RTV) silicone. The material has been in regular production for use in DOE components and assemblies since 1977.

Several studies carried out at the Allied-Signal Kansas City Plant (Schicker et al. 1995) addressed the effectiveness of the getters in removing hydrogen under controlled conditions. A number of gases, including CO, N_2O and NH_3, were subjected to the getters with hydrogen and nitrogen gas present. N_2O and NH_3 did not affect the performance of the catalyst. Carbon monoxide at a concentration of 1 percent was found to reduce the rate of reaction somewhat, but not to irreversibly poison the catalyst. These experiments did not address any VOCs present in TRU waste headspace gases.

The DOE Stockpile Stewardship Program has a number of projects currently being funded addressing the reactivity and characterization of getters. At a recent Joint Working Group (JOWOG) meeting in Livermore, California, a number of papers on getters including DEB were presented including two papers addressing this project. As a result of the workshop, the project team will be able to coordinate their kinetic studies with complimentary studies supported by Stockpile Stewardship. This will provide a significant forum to address poisoning issues as well as engineering issues when that phase of the project is developed.

During the first phase of the Hydrogen Getters Project, the primary objectives were to develop and test an experimental procedure that would be used to study the kinetic behavior of getters, to identify potential poisons and inhibitors, and to study the effects of potential poisons and inhibitors on the ability of getters to remove hydrogen. Also, a kinetic model was developed and tested for use as a predictive tool that would calculate the effects of adjusting experimental parameters (flow rate, temperature, contaminants, etc.) on the rate and capacity of the getters..

At the end of Phase I, several endpoints were attained:

- The experimental apparatus was successful in testing the getters' ability to remove hydrogen with

or without poisons or inhibitors present.

- The chlorinated hydrocarbons were shown to be poisons for the DEB/Pd/C mixture.
- Preliminary tests using Tedlar as a packaging material showed that it would preferentially block carbon tetrachloride from poisoning getters reactions.

The kinetic model was successful in qualitatively predicting the getters' reactivity as a function of experimental parameters.

2.4 Technology Improvements

DEB has been proven reliable in reacting irreversibly with hydrogen gas. To justify the use of DEB for removing hydrogen from the headspace of TRU waste, DEB must be demonstrated to be effective in the presence of other gases also known to be present in TRU waste.

If these tests demonstrate the effectiveness of DEB, further improvements to DEB technology will need to be addressed during the next phase of the project. The next phase will focus on engineering aspects (physical form, amount, location of placement) related to actual use for TRU waste shipments.

3.0 REQUIRED DATA AND ACQUISITION APPROACH

Permeability Testing

Preliminary experiments indicate that hydrogen is significantly more permeable through Tedlar than is carbon tetrachloride. Thus it is possible that using Tedlar as a packaging material for the getter could protect the getter from the posionous effects of halogenated VOCs while allowing hydrogen to be catalytically removed from the headspace.

During Phase II, permeability testing will be carried out with Tedlar and similar materials under a number of experimental conditions. Permeability through these materials will be tested for a set of chlorinated organic compounds and carbon monoxide relative to the permeability of hydrogen.

Alternate Getter Systems

Preliminary studies with DEB/Pd/alumina as an alternative to DEB/Pd/C have shown that carbon tetrachloride does not poison the getter reactions with alumina as the co-catalyst. However, this formulation is significantly less effective as a hydrogen getter. Further testing will be necessary to clarify whether the benefits of this material being immune to poisoning outweighs the downside of it being less reactive towards hydrogen.

The results strongly suggests that the chlorinated hydrocarbon is physically or chemically absorbing to the activated carbon co-catalyst and that this absorption is impeding the movement of reactive species to the active catalyst sites (or possibly preventing the formation of the activated complex or intermediates necessary for gettering).

Further studies with alternate getter systems will be carried out as part of the Phase II experiments. Other candidate getter systems are mixtures of DEB and 60% Pd-40% Cu alloy dispersed on either carbon or alumina substrates.

Optimization of Kinetic Model

Preliminary studies using a kinetic model to simulate the getter reactions have shown to qualitatively predict the effects of poisons, inhibitors, temperature, and flow rate on the gettering rates and

capacities. With the additional experiments addressing semi-permeable membranes and alternate getter systems, it is more important to be able to quantitatively predict these effects. In order to make these predictions, the kinetic model will be modified, tested, and deployed to allow for the optimization of the experimental parameters. This optimization will generate a set of rate constants for a proposed gettering mechanism that will be statistically consistent for a set of experimental conditions. These rate constants can then be used to predict gettering rates and capacities for other experimental conditions.

Drum-Scale Tests

After the alternate systems and semi-permeable materials have been tested and the model has been used to optimize rate constants and quantitatively predict effects of experimental parameters on the gettering rates and capacities, drum-scale tests will be carried out to demonstrate the getters' effectiveness in meeting the 5% hydrogen limit for TRUPACT-II containers. These tests will be used to determine the optimum getter package for the various containers and associated contaminants, the amount of getter needed to achieve the 5% limit over the 60-day transportation period, the optimum placement of the getter package, and the quality assurance necessary to insure the effectiveness of the getter package.

4.0 TEST OBJECTIVES

See Section 3.0

5.0 DATA QUALITY OBJECTIVES

Inasmuch as the research is largely exploratory (alternative getters, suitable packaging materials, model optimization and refinement), numerical data quality objectives cannot be readily specified. At this stage of technology development we are primarily searching for qualitative indications of improved hydrogen gettering performance in the presence of chlorinated VOCs through the use of alternative catalysts and suitable packaging materials.

6.0 DATA ACQUISITION DESIGN

See Section 7.0

7.0 DESIGN OF EXPERIMENTS

Permeability Testing

During Phase II, permeability testing will be carried out with Tedlar and similar materials under a number of experimental conditions. Permeability through these materials will be tested for a set of chlorinated organic compounds and carbon monoxide relative to the permeability of hydrogen.

A simple permeability test cell will be constructed consisting of two air-filled chambers separated by a Tedlar membrane. A test gas of hydrogen and a chlorinated VOC will be introduced into one chamber. The rate of increase in the concentrations of the test gases in the other chamber will be direct measure of the permeability of the tedlar to the test gases.

The permeability constants will be used in conjunction with the kinetic model to predict getter performance under various deployment scenarios.

Alternate Getter Systems

Further studies with alternate getter systems will be carried out as part of the Phase II experiments. Other candidate getter systems are mixtures of DEB and 60% Pd-40% Cu alloy dispersed on either carbon or alumina substrates.

Using our flow system for measuring reaction kinetics, experiments will be carried out with these alternate systems as a function of hydrogen flow rate, temperature, and presence of potential poisons and inhibitors. The gettering rates and capacities will be determined by comparing the hydrogen mole fraction output through the reaction vessel for the alternate systems and the DEB/Pd/C system and by using the kinetic model to differentiate between rate and capacity effects.

Optimization of Kinetic Model

Preliminary studies using a kinetic model to simulate the getter reactions have shown to qualitatively predict the effects of poisons, inhibitors, temperature, and flow rate on the gettering rates and capacities. With the additional experiments addressing semi-permeable membranes and alternate getter systems, it is more important to be able to quantitatively predict these effects. In order to make these predictions, the kinetic model will be modified, tested, and deployed to allow for the optimization of the experimental parameters. This optimization will generate a set of rate constants for a proposed gettering mechanism that will be statistically consistent for a set of experimental conditions. These rate constants can then be used to predict gettering rates and capacities for other experimental conditions.

In order to carry out these optimizations, experimental data sets will be used in a least squares fit to theoretical data sets, and the model input parameters will be adjusted through a Monte Carlo random walk fashion to minimize the least squares fit function. Between 100 and 200 data points will be used in the least squares fit function to insure statistical relevance. A digitizer and interpolator will be used to generate the experimental data points for each comparison.

Once a set of rate constants has been quantitatively determined, the model will then be used to predict rate and capacity effects under different experimental conditions. This will be useful in determining the effect of including semi-permeable materials or altering the getter system to minimize poisoning. The model will also be tested in the Drum-Scale Test described below.

Drum-Scale Tests

After the alternate systems and semi-permeable materials have been tested and the model has been used to optimize rate constants and quantitatively predict effects of experimental parameters on the gettering rates and capacities, drum-scale tests will be carried out to demonstrate the getters' effectiveness in meeting the 5% hydrogen limit for TRUPACT-II containers. These tests will be used to determine the optimum getter package for the various containers and associated contaminants, the amount of getter needed to achieve the 5% limit over the 60-day transportation period, the optimum placement of the getter package, and the quality assurance necessary to insure the effectiveness of the getter package.

8.0 INSTRUMENTATION, PROCESS MONITORING, AND CONTROL DESIGN

Figure 8-1 provides a process flow diagram for the bench-scale experiments on alternate getter systems conducted for this study. The same basic process will be used for the drum scale test with a 30 gallon drum replacing the column indicated in Fig. 8-1.

9.0 RUN PLAN SUMMARY

Permeability Testing

Gases to be tested:
- hydrogen
- carbon tetrachloride
- carbon monoxide
- possibly halogentated VOCs

Materials to be tested:
- tedlar
- possibly other materials

Alternate Getter Systems

Candidate Getter Systems to be tested :
- DEB with Pd-Al2O3
- DEB with Pt:Ru-C
- DEB with other noble metal catalyst systems

Optimization of Kinetic Model

Rate constants at constant flow and temperature conditions, variable getter mass
Rate constants at constant getter mass, and flow, variable temperature.
Adaptation from dynamic to static conditions to simulate drum conditions.

Drum-Scale Tests

DEB with Pd-C in drum with constant source of H2.
- in both a nitrogen and air atmosphere
- with and without CCl4
- with & without tedlar packaging

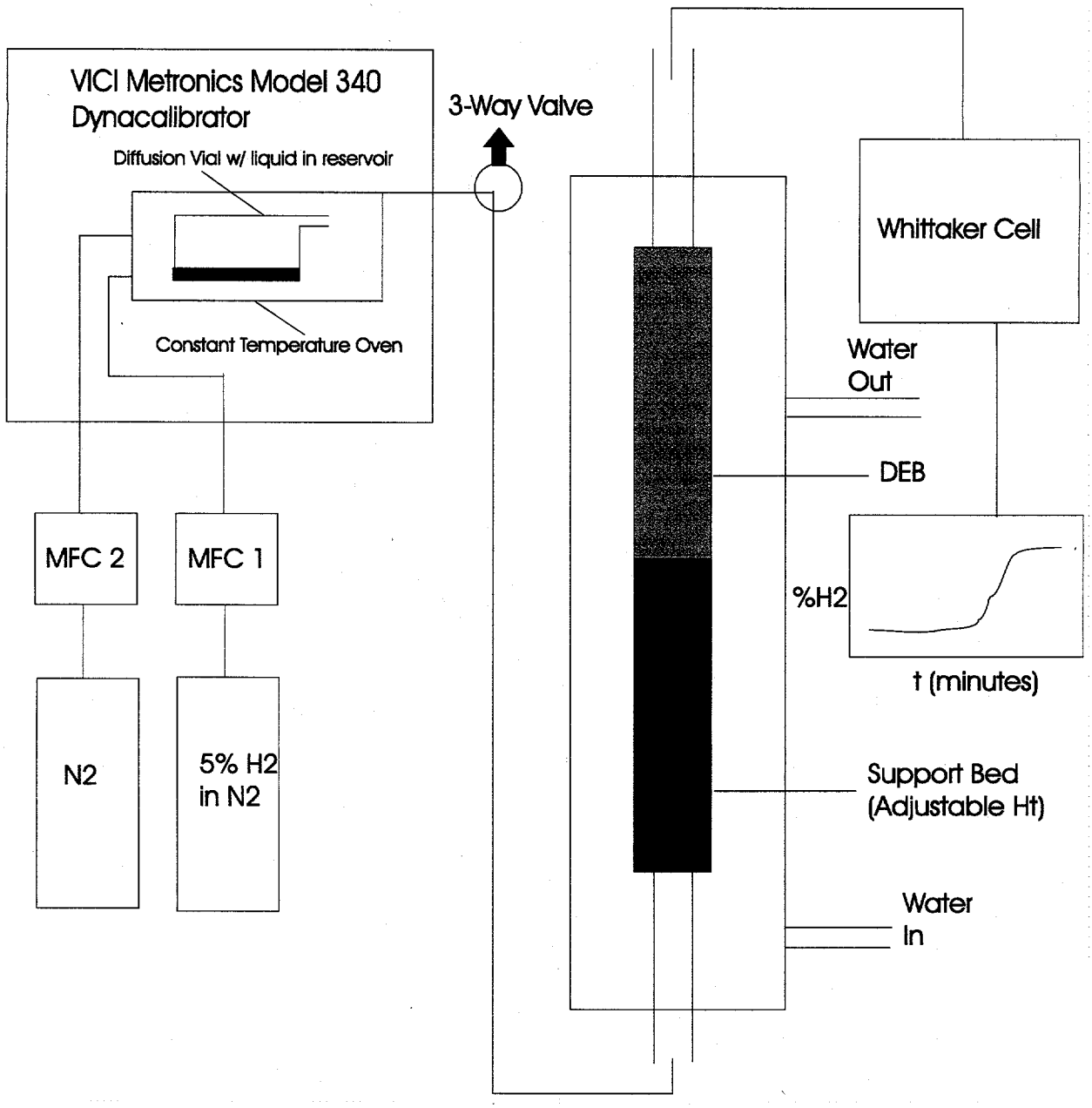

Figure 8-1. Process Flow Diagram

10.0 DATA ANALYSIS

Data from the experiments described above will be examined for evidence of improved getter performance in the presence of chlorinated VOCs.

11.0 SUPPORT REQUIREMENTS

All experiments will be conducted by the LANL Chemical Sciences and Technology Division. The Principal Investigator is Dr. Eugene Mroz ([505]-667-7758, mroz@lanl.gov). Support staff includes trained mechanical, electronics, and chemical technicians as well as undergraduate and graduate student technical assistants.

No special facility requirements are anticipated for carrying out this study. The facility (TA-48, Building RC-1) is a multifunctional chemistry laboratory. The laboratory within this facility (Room 306) is a standard chemistry laboratory equipped with the necessary bench space, fume hoods, and utilities for these experiments.

All gas stream analyses for hydrogen will be conducted on-line, in real time, by an electronic sensor. LANL does not anticipate a need for shipping samples to other laboratories for analysis.

Materials used for these experiments include the following:

- *DEB Hydrogen Getter.* LANL is obtaining this material from the manufacturer, Allied-Signal, Kansas City Plant, and will use their standard formulation of the product which is 75 percent DEB and 25 percent catalyst. The catalyst is 5 percent Pd on carbon. DEB is prepared in powder form (mesh size: -14 to +50).

- *Certified gas mixture of 5 percent hydrogen in nitrogen.* Several commercial sources are available.

- *Organic compounds.* Small amounts (a few grams) of several different, but readily available, organic compounds will be used to generate test gas mixtures.

The primary waste products will include consumed DEB getter materials and small amounts of unused organic compounds. These will be disposed of in accordance with facility waste management practices.

There will be no need for facility decontamination, decommissioning, or equipment disposal as a result of these experiments.

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