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An Issue Paper on the Use of Hydrogen Getters in Transportation Packaging

P. J. Nigrey

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AN ISSUE PAPER ON THE USE OF HYDROGEN GETTERS IN TRANSPORTATION PACKAGING

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Abstract

The accumulation of hydrogen is usually an undesirable occurrence because buildup in sealed systems pose explosion hazards under certain conditions. Hydrogen scavengers, or getters, can avert these problems by removing hydrogen from such environments. This paper provides a review of a number of reversible and irreversible getters that potentially could be used to reduce the buildup of hydrogen gas in containers for the transport of radioactive materials. In addition to describing getters that have already been used for such purposes, novel getters that might find application in future transport packages are also discussed. This paper also discusses getter material poisoning, the use of getters in packaging, the effects of radiation on getters, the compatibility of getters with packaging, design considerations, regulatory precedents, and makes general recommendations for the materials that have the greatest applicability in transport packaging. At this time, the Pacific Northwest National Laboratory composite getter, DEB [1,4(phenylethylene)benzene]or similar polymer-based getters, and a manganese dioxide-based getter appear to be attractive candidates that should be further evaluated. These getters potentially can help prevent pressurization from radiolytic reactions in transportation packaging.

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INTRODUCTION

Materials referred to as getters, degassers, absorbers, or scavengers[1-3] are being used to control gas in vacuum tubes, glove boxes, and vacuum systems. The use of getters in transportation packaging, however, thus far has been extremely limited. These materials have the capability to chemically bind the gases within themselves rather than by physical surface adsorption. The chemical bonds formed during the reaction of the gas with the getter material may vary in strength. In situations where chemical reactions have occurred during the gas adsorption process, i.e., where the getter material is transformed from the original composition to a new composition, strong chemical bonds are typically formed, and the getter is referred to as an irreversible getter. When the adsorbate gas forms a weakly bonded complex with the getter material, the getter is referred to as a reversible getter. The distinction between these getter materials is that reversible getters, upon the appropriate physical treatment, will revert to their original composition, allowing them to be regenerated and reused. The regeneration in all cases is accomplished by supplying sufficient thermal energy (heating) to decompose the weakly bonded getter/adsorbate complex. For example, with reversible getters, gaseous adsorbates such as water vapor, carbon dioxide, nitrogen, and hydrogen and its isotopes form hydrates, carbonates, nitrides, and hydride (deuteride or tritide) compositions. Because both reversible and irreversible getters consume the gaseous species to form a new solid composition, the net process in sealed systems such as packaging is a reduction in the partial pressure. This is a desirable effect in sealed systems where gases are generated from radiolytic or thermal processes. A dramatic example of such pressure reduction is the use of getters in the production of ultrahigh ($>10^{-9}$ Torr) and ultraclean vacuum.[4] Because the main purpose of this paper is to discuss the potential use of getters for the mitigation of vessel pressurization that arises from radiolytic hydrogen production in transportation packaging, the remainder of the discussions will focus on hydrogen or tritium getter materials.

The accumulation of hydrogen is usually an undesirable occurrence because hydrogen buildup in sealed systems poses explosion hazards under certain conditions. Hydrogen scavengers, or getters, can avert these problems by removing hydrogen from these environments. Hydrogen and its isotopes can react with various chemical compounds to form hydrogen-rich chemical compounds, and when such compounds are formed with metals, they are referred to as metal hydrides.[5] Alternatively, chemical compounds that contain unsaturated carbon-carbon bonds, such as alkenes (carbon-carbon double bonds) and alkynes (carbon-carbon triple bonds), as part of their chemical composition can form saturated carbon-carbon bonds or alkanes (carbon-carbon single bonds) when catalytically reacted with hydrogen. Such reactions, however, are not spontaneous at ambient temperature and pressure in the absence of a catalyst. Typically, such reactions only occur in significant rates at elevated temperatures (>100°C), high pressures (>100 atmospheres), and in the presence of specific catalysts. These hydrogenation catalysts include the previously mentioned metal hydrides as the catalytic intermediate. The most prominent metal hydrides used in such reactions are precious-metal hydrides such as ruthenium, rhodium, and palladium hydride. However, most of these catalytic reactions are homogeneous[6] in nature, i.e., the hydrogenation reactions occur in solution. Heterogeneous catalysis (catalysis occurring at the solid/gas interface) is used extensively in the petrochemical industry for petroleum refining. Since the potential pressurization occurring during the transportation of plutonium-

bearing materials will originate from solid/gas reactions, heterogeneous reactions must be considered. Such reactions form the basis of all hydrogen getter materials response, whether they are reversible or irreversible.

In contrast to the previously described undesirable aspects of accumulated hydrogen, hydrogen storage in metal hydrides is an ultimate goal in hydrogen-fuel-powered vehicles. The efficient usage of getters in these applications relies on materials that exhibit high hydrogen-to-metal ratios with complete reversibility of hydrogen adsorption/desorption at relatively low temperatures.

The getter scavenges hydrogen in a chemical reaction, and all chemical reactions are driven by a combination of thermodynamic and kinetic factors. The component that drives the speed of a reaction produces the kinetics of that reaction. Kinetics of chemical reactions usually exhibit Arrhenius behavior, i.e., they are activated by temperature. With increased temperature, increased reaction rates are typically observed. Depending on the type of getter material involved, there exists an optimum temperature range for optimum getter performance. In the case of reversible getter materials, that optimum temperature range usually spans several hundred degree centigrade, while the irreversible getters are restricted to temperatures near 100°C. Since the optimum hydrogen gettering temperature is dependent on the specific material, it is not possible to be more specific here. A discussion of temperature effects on getter performance will be made when specific hydrogen getters are described later in this report. It should be noted, however, that the optimum temperature is determined by the decomposition temperature of the getter/adsorbate complex. For reversible metal hydride getters, the decomposition temperature of the metal hydride provides some indication of the maximum temperature at which these materials can be used without significantly decreasing gettering performance. For these materials, decomposition temperatures in excess of 500°C are typical. For irreversible systems involving organic compounds, decomposition temperatures are usually more than 150°C. The obvious explanation for these relatively low decomposition temperatures is that virtually all organic compounds undergo some thermal degradation at temperatures approaching 200°C. Thus, depending on the expected normal conditions of transport of a package, the selection of either irreversible or reversible hydrogen getter materials may be required. If expected temperatures are considerably below 150°C, irreversible getters may be appropriate. The opposite is certainly required when normal transport conditions exceed that temperature. Another selection criterion for getters will be the potential poisoning effect on getter materials of specific small molecular species. This issue and its effect on getter performance will be discussed in some detail in a subsequent section.

REVERSIBLE GETTER MATERIALS

The basis for the absorption of hydrogen by metals lies in the physiochemical properties of hydrogen. A key aspect of the chemistry of hydrogen is its dissociation and chemical bonding. The highly endothermic (heat absorbing) dissociation process for hydrogen provides an explanation for its low reactivity at low temperatures. When catalyzed by transition-metal species, low reaction temperatures are possible because of the lower dissociation energy of the

catalyzed reactions. The catalyzed reactions are thought[7] to involve the splitting of hydrogen to form a hydride ion (H^-), which binds to the metal catalyst. The hydride ion exists in saline (alkali) hydrides such as sodium and calcium hydrides. In contrast to hydrogen's ability to form ionic bonds with certain metals, the majority of metal hydrides contain an electron-pair bond, i.e., a hydrogen bond that has considerable covalent character. Thus the ability of hydrogen to exhibit a unique bonding arrangement with metals leads to numerous compounds, often non-stoichiometric in character discussed next.

In the case of transition metals, hydrogen reacts with these metals or their alloys on heating to yield compounds commonly called hydrides, even though in some cases they do not contain hydride ions. Many of these metal hydride systems are very complicated, involving the existence of more than one phase and different stoichiometries. The most extensively studied systems involve highly electropositive elements, such as the lanthanides and actinides, and the titanium and vanadium groups of the d-block transition metals. Titanium, zirconium, and hafnium absorb hydrogen exothermically (heat evolved) to give materials such as TiH_2 and $ZrH_{1.9}$. The affinity of many of the other d-block elements for hydrogen is small, with the exception of metallic palladium.[8] In fact palladium was the earliest[9] recorded metallic absorber of hydrogen where the hydrogen-to-metal ratio was close to one. Since actinide hydrides are formed by heating the metal in a hydrogen environment, it is useful to mention that uranium metal reacts rapidly and exothermically with hydrogen at 200 to 300°C to give a pyrophoric black powder. Thus, elevated temperatures are typically involved to obtain high absorption rates. The adsorption reactions are reversible with the hydride decomposing at slightly higher temperatures to give reactive and extremely fine metal powders. A practical application of this reaction by uranium is its use in a tritium transport vessel,[10] i.e., its use as a tritium getter. In fact, there is information available that describes the use of uranium as a tritium getter in fusion technologies.[11]

In the following discussions, selected types of hydrogen getters are described. The selection was based on good gettering performance in certain applications or potential for improved performance. The composition of intermetallic compounds can be generically described as AB, A_2B, and AB_5-types, where A and B represent different metals.

Intermetallic Zirconium System

Intermetallic compounds such as zirconium-cobalt (ZrCo) and zirconium-iron-vanadium [$Zr(FeV)_2$] have recently been studied as hydrogen getters.[12-17] ZrCo is an example of a binary intermetallic compound and has been described as a replacement for uranium as tritium getter.[12] It has also been reported as a new hydrogen getter in Lyman-α radiation sources.[13] A number of these intermetallics have the decided advantage over uranium in that their hydrides are much less pyrophoric than powdered uranium metal and its hydrides. ZrCo was also reported to exhibit up to 35 loading/deloading cycles at room temperature without loss in storage capacity or change in hydriding characteristics.[14] The intrinsic stability of the completely hydrided phase, $ZrCoH_3$, is indicated by the very low hydrogen pressure produced by its dissociation at room temperature.

An example of a ternary intermetallic compound is $Zr(FeV)_2$. It has been suggested[15] that this ternary intermetallic getter can be used for tritium removal in high-field fusion machines. A number of these binary and ternary intermetallics are manufactured by SAES Getters, Milan, Italy or Ergenics, Inc., Ringwood, NJ. In the case of the ternary intermetallic, several alloys are available, with St737[16] most closely resembling the elemental composition required for $Zr(FeV)_2$.

Similar to uranium getters, zirconium alloys require high temperatures (> 300 - 400°C) to initially produce the activated getter, i.e., a getter having optimum hydrogen sorption capacity. Typically, evacuation is also required during the activation procedures to remove volatile chemical species. While the intermetallic compounds may be used with minimal or no activation steps, optimum storage capacity and hydriding kinetics are obtained after thermal activation. A partial explanation is that activation produces powders with small grain sizes having large surface area. For this reason, zirconium-based getters find ready application in high vacuum operation. Here removal of low molecular weight gases, i.e., oxygen, nitrogen, hydrogen, is the main concern since the highly reactive getter will form metal oxides, nitrides, carbides, and hydrides. While metal carbides are least reversible upon heating, the relatively low thermal stability of metal hydrides provides a fair degree of reversibility, especially at higher temperatures and low pressures in the presence of hydrogen. Accidental introduction of air onto $ZrCoH_3$ results in self-accelerating reactions above 200°C. For example, the lowest temperature for a sustained self-accelerating reaction is 227°C and 727°C, respectively, for oxidation or nitriding to occur in $ZrCoH_3$.[17]

PNNL Composite Getter

SAES Getters manufactures binary zirconium-based getters; however, the reactivation or regeneration of zirconium getters must be performed at high temperature in a vacuum or under an inert gas. Researchers at Pacific Northwest National Laboratories (PNNL)[18] have recently described an all-metallic, air-operable, composite getter for hydrogen that can getter hydrogen in air or an inert atmosphere at ambient or elevated temperatures. PNNL has completed a year of engineering/fabrication development and performance testing for both absorption kinetics and capacity. The primary target application is mitigation of hydrogen gas generation in waste storage drums during shipment, or dry spent fuel storage casks, with the goal to maintain container atmosphere at < 5% H_2.

PNNL describes its getter design as follows:

> The PNNL Composite Getter design is an all-metal, coated zirconium-based getter, with the metal coating providing a protective oxygen barrier while simultaneously allowing transport of hydrogen. A specific deposition method with specific parameters is used to lay down the protective metal layer of specific thickness. The coating minimizes passivation of the getter in air, oxygen, or moisture. The getter is shown to work in air at ambient temperature to 150-200°C. The measured hydrogen gettering rate, based on present data to date, ranges from 25 -50 cc STP/day/kg (0.025 – 0.050 cc STP/day/g) of

getter directly in air. In inert atmosphere, such as in depleted spent fuel casks, the rate is higher by a factor of 1000. The hydrogen loading capacity of the getter is measured at 160 liters STP/kg (0.160 liters STP/g) of getter, regardless of atmosphere. With the coated two-piece getter design, it is currently believed that potential contaminating gases, such as halogenated volatile organic hydrocarbons, carbon monoxide, or moisture, will not affect getter kinetics or capacity, since the atmosphere never comes in contact with the actual getter surface.[18]

Magnesium Nickel System

Magnesium and magnesium alloys are extremely attractive as hydrogen getters because they can store more hydrogen by weight (3.6%) than most metal hydrides. However, the hydriding and dehydriding kinetics of magnesium are slow and the hydride is too stable for most practical hydrogen storage applications. By alloying with various additives, the kinetics can be improved at the expense of a reduction in the storage capacity.[19] The theoretical volume density of magnesium hydride is high (100-115 kg/m^3) and exhibits long stability. The previously mentioned kinetic limitations can be overcome by coating the metal alloy with a high hydrogen permeability material such as palladium and by using nanometer size particles. Thus very fine particles of magnesium alloy, having a metal coating selected for compatibility during the hydride phase change expansion, would be expected to exhibit high volume efficiency and hydriding kinetics.

Lanthanum-Nickel System

Lanthanum pentanickel is a lanthanum-nickel alloy representing a class of AB_5-type materials. These AB_5-type hydrogen storage materials have some inherent advantages in contrast to the other types discussed previously, e.g., easy activation capability at ambient temperature, fast reactivity at ambient temperature and pressure, and tolerance to gaseous impurities. Multiphase compositions of this material have exhibited ~1.6 wt.% hydrogen storage capacity.[20] This storage capacity was the highest reported value for the $LaNi_5$ system.

Graphite Nanofibers

In contrast to hydrogen storage by formation of metal hydrides, the storage of hydrogen could also involve for the adsorption on various solids including carbon at cryogenic conditions. Since cryoadsorption requires extremely low temperatures, i.e., liquid nitrogen temperatures, such materials would not lend themselves readily to use in nuclear materials transportation vessels. However, the search for surface adsorbing media for hydrogen storage at room temperature has recently focused on graphite nanofibers. The preliminary report[21] indicates that the solid absorber consists of very small graphite platelets, 30-500Å in width, which are stacked in a perfectly arranged conformation. It was found that the material is capable of adsorbing and retaining in excess of 20 L (STP) of hydrogen per gram of carbon when the nanofibers are exposed to the gas at pressures of 120 atm at 25°C. This value is over an order of magnitude higher than that found

with conventional hydrogen storage systems. In view of the conceptual similarity between graphite nanofibers and a novel class of carbonaceous materials such as fullerenes,[22] it is tempting to envision similar and possibly greater hydrogen storage under these conditions.

As should be noted from the previous discussions, the described hydrogen getters exhibit reversibility in absorbing hydrogen. While this particular property of the getter is extremely important for vacuum and hydrogen-fuel storage applications, the reversibility of hydrogen gettering by the getter material is less of an issue when applied in packagings for the transportation of nuclear materials. The one-time usage of these materials, especially if storage of the nuclear materials is envisioned after the transportation campaign, would place less emphasis on the reversibility of hydrogen adsorption/desorption. In fact, an argument could be made that irreversible gettering materials are more appropriate for transportation packaging applications. Getters of this type will be discussed next.

IRREVERSIBLE GETTER MATERIALS

Alkali-Metal Graphite Intercalation Compounds (AGIC)

Alkali metals such as potassium, rubidium, and cesium react with graphite[23] to form complexes analogous to alkali salts, i.e., $K^{+}C_{8}^{-}$. The alkali metal effectively reduces the graphitic structure. The intercalation process by an alkali-metal involves insertion of the cation between the sheets of the graphite structure. The sorption and desorption of hydrogen by AGIC have recently been studied.[24] These studies showed that hydrogen, oxygen, and carbon monoxide can be gettered by AGIC. Extremely large pumping selectivity for oxygen in a hydrogen-rich environment was found. However, the high reactivity of AGIC in air would require the presence of an inert atmosphere for operation as hydrogen getters.

Manganese Dioxide/Silver Oxide/Calcium Oxide System

This material has been described as a useful tritium-getter for absorber rods in the transport and storage cask CASTOR BARRE.[25] Manganese dioxide that has been catalytically activated with silver compounds exhibits excellent oxidizing capabilities for the cold burning of hydrogen even at ambient conditions. Laboratory experiments at the Nuclear Research Center KFA in Jülich were performed to optimize the reaction material with respect to its capacity and reaction kinetics. According to the results of the experiments,[25] the reaction sequence can be described as follows: Molecular hydrogen is catalytically dissociated at the contact surface between the manganese dioxide and the silver oxide particles. The hydrogen radicals formed by the catalysis then reduce the manganese dioxide (MnO_2) particles to manganese sesquioxide (Mn_2O_3), forming water in the process. Calcium oxide, a desiccating agent that is incorporated into the getter, removes the water that is formed by this reaction and any water vapor by forming calcium hydroxide. Laboratory tests demonstrated that the reaction material performed well at absorbing tritiated hydrogen (HT) and tritiated water vapor (T_2O or TOH). As can be seen, the formulated material is a combination getter, i.e., a hydrogen and moisture getter. In a sense this material is a form of recombiner. A similar approach has been suggested[26] for 1,4-bis(phenylethynyl)benzene (DEB) mixed with lithium or calcium hydride.

DEB System

DEB is an example of a crystalline organic hydrogen getter that will irreversibly remove hydrogen by the catalytic hydrogenation of carbon-carbon double or triple bonds in the getter. This material was first developed at Sandia National Laboratories in the late 1970's.[27] The Honeywell Federal Manufacturing & Technologies, formerly the Allied-Signal Kansas City Plant, has had extensive experience in crystalline organic getter technology since 1978 by developing organic getters for the Department of Energy (DOE) Nuclear Weapons Complex.[28] The compound DEB represents the fourth generation of getter development and is the standard DOE production hydrogen getter material. DEB is a nontoxic, nonmutagenic, crystalline, white solid that, when formulated with various catalysts, makes an irreversible hydrogen trap. The standard getter formulation has a capacity of 241 cc (STP) hydrogen per gram of getter. Pure DEB melts at 179°C, and fully hydrogenated 1,4-bis(phenylethynyl)benzene melts at 87°C. The reduced product remains solid to at least 80°C. The reduction is exothermic, and its hydrogenation rate increases with hydrogen pressure. The getter works over a wide temperature range, although the hydrogen uptake is slower at low temperatures. The irreversible reduction of DEB getters is shown in the following equations:

$$4H_2 + DEB \rightarrow DEB(H_8)$$

$$4H_2 + R\text{-}C{\equiv}C\text{-}R\text{-}C{\equiv}C\text{-}R \xrightarrow{\text{Pd on C}} R\text{-}CH_2\text{-}CH_2\text{-}R\text{-}\ CH_2\text{-}CH_2\text{-}R$$

where R is a phenyl group. If the melting point of the reduced DEB product has the potential for introducing an operational constraint in a package, higher temperature versions of DEB, developed at Sandia are available.[29]

By weight the standard formulation consists of 75% DEB and 25% catalyst (5% palladium on carbon). Other formulations have been used for different applications, but this material represents the best balance between reactivity and cost. These materials effectively scavenge hydrogen, deuterium, and tritium. They usually use up more than 90% of their capacity when exposed to high or low concentrations of hydrogen and have been shown to be stable in the absence of hydrogen for up to 18 months (70°C, nitrogen). When excess getter at room temperature is used, residual hydrogen concentrations are reduced to < 10 ppm. Other hydrogen getter materials based on DEB have been formulated including polyethylene composite, urethane adhesive, and RTV castable silicone. In addition, polymer-based hydrogen getters, that rely on homogeneous catalytic hydrogenation of unsaturated organic polymers have been reported.[30] These getters use an iridium-based catalyst because of its high activity in hydrogenation and its resistance to oxygen poisoning. Hydrogenation can be an extremely rapid reaction. Under ideal conditions, > 90% of the hydrogen in the volume that contains the getter can be scavenged in 2 seconds. These rapid reactions occur only in the absence of other gases with a degassed getter; in the presence of air, the reaction is slower. More recently, Shepodd[31] has patented polymer-based recombiners that utilize palladium dispersed on carbon as a hydrogenation catalyst. In many applications, a slower reaction is desirable to prevent the melting or sintering of the getter caused by the high exothermicity during rapid reactions. To avoid the sintering during rapid

uptake of hydrogen, diluting the getter with inert material such as in a polymeric composite can be another strategy. As was mentioned above, DEB can be formulated into a combination hydrogen, water and oxygen getter especially for maintaining a dry, inert atmosphere over long periods in sealed containers. The combination getters contain water scavengers such as lithium hydride or calcium hydride. In essence, this approach is analogous to the $MnO_2/Ag_2O/CaO$ system described above. This approach has also been proposed by SAES to getter various gases at relatively high gas pressures. A further discussion of this type of a getter is presented below.

Cobalt Oxide/Calcium Oxide/Barium-Lithium Alloy

SAES getters laboratories have developed a novel gettering system called the COMBOGETTER™, which is made up of three different active materials.[32] This commercial getter is similar to the previously described manganese oxide/silver oxide getter and consists of a combination of three different getter materials integrated in a single construct. The cobalt oxide provides an efficient sorption speed and capacity for hydrogen. the calcium oxide component is a highly efficient dessicant that intercepts and adsorbs moisture, and the barium-lithium alloy adsorbs nitrogen and other active gases such as oxygen and carbon dioxide. In addition, these three component materials adsorb gases at room temperature. Short air exposure up to 15 minutes is reported by SAES not to affect the getter's adsorption characteristics. While the literature available from SAES recommends evacuation of the environment in which the COMBOGETTER™ resides, conversation with representatives of SAES suggests that the getter might be used at atmospheric pressures. To determine whether this is actually the case, the getter will need to be evaluated under transportation conditions such as elevated temperatures and pressure. However, it should be obvious that the adsorption of gases in a closed systems could lead to a significant reduction in pressure, i.e., produce a vacuum in the primary container. The obvious advantage of this type of a gettering system is the removal of potential poisons to the active hydrogen gettering material, cobalt oxide. A further discussion of this topic follows.

POISONING GETTER MATERIALS

Since metal hydrides are the active ingredient in certain getters, any formation of compounds other than metal hydrides leads to less adsorption capacity for hydrogen, which results in the deactivation or the poisoning of getters. Thus the formation of metal oxides, nitrides, carbides, sulfides, or other metal compounds within a reversible getter as a result of reactions with oxygen, nitrogen, carbon oxides, and sulfur compounds could lead to a decrease in capacity and reversibility. The formation of thermally stable oxides, nitrides, carbides, and sulfides leads to decrease adsorption of hydrogen. Depending on the composition of the getter, this poisoning may be limited because the hydriding reaction predominates, i.e., favorable thermodynamics. This is especially true if formation constants are significantly different at lower temperatures. Additionally, if the poisoning agents are only chemisorbed on the surface of the getter, the getter may be reactivated. If elevated temperatures exist, the migration of the poisoned surface into the bulk of the getter could also result in the regeneration of a fresh surface. Thus, depending on the composition of the hydrogen getter, poisoning may or may not lead to decreasing hydrogen adsorption. Generally speaking, intermetallic iron-titanium alloys have been reported to suffer the most from poisoning reactions, while lanthanum-nickel alloys are relatively tolerant to

poisoning. An understanding of the deactivation of intermetallic hydrogen getters involves understanding the mechanisms of activation for hydrogen absorption. A mechanism that has the greatest support for the activation process for the case of $LaNi_5$ and possibly for Mg_2Ni is the surface segregation and catalysis model. Other mechanisms include oxide layer cracking, permeability of surface oxide layers, and oxide layer dissolution mechanisms. Irrespective of which mechanisms are operational in intermetallic hydrogen getters, the ability of hydrogen to readily form metal hydride will determine the rate that hydrogen is absorbed. In the following discussions, available information on the poisoning of hydrogen getters will be presented. Since the effects of various poisons on all the above materials have not been extensively examined, the discussions here will center on selected hydrogen getters where such information was available in the literature.

Zirconium-Cobalt System

Zirconium alloy getters such as Zr_2Fe at operating temperatures of 300-400°C have been reported[33] to be essentially chemically inert to nitrogen. In addition, the alloy is not highly sensitive to impurities such as carbon monoxide, carbon dioxide, and ammonia. The inertness of Zr_2Fe to these reactions is notable since zirconium metal itself reacts near 400°C with common contaminant gases such as oxygen, nitrogen, carbon monoxide, and carbon dioxide present in hydrogen streams.[34] Since ZrCo, a most promising getter for replacing uranium as a getter[35] is similar to Zr_2Fe, it may manifest a resistance to poison similar to that of the zirconium-iron alloy. Indeed, with ZrCo no reactions were reported to occur with nitrogen at normal operating temperature.[36] At least at 300°C, the poisoning of ZrCo by nitrogen, carbon monoxide, and oxygen is not accompanied by a significant reduction in the reaction rate with hydrogen.[37] Passivation at room temperature of metals and metal alloys is known to occur when the permeation of hydrogen atoms through existing surface oxide layers becomes rate determining. These results suggest that reactions by ZrCo with these gases inhibit rather than prevent hydrogen adsorption.

Magnesium-Nickel

The effects of foreign gases such as oxygen, nitrogen, carbon monoxide, and carbon dioxide have been studied for magnesium.[38] Since studies concerning the poisoning of the intermetallic magnesium-nickel compound itself thus far have not been identified, the discussion here will deal with the effects of the main component in the intermetallic compound, i.e., magnesium. The effects of the four gases on magnesium were different:

- oxygen reacted heavily with the metallic magnesium, but still allowed the formation of hydride at a reduced rate.
- nitrogen caused a slow-down in adsorption speed, but left the metal powder almost unchanged after desorption.
- carbon monoxide practically prevented hydrogen uptake.
- carbon dioxide in a concentration of 2% totally prevented hydrogen uptake in magnesium.

It is interesting to note, however, that other potential poisons, such as halogens, can act as catalytic agents that can lead to the formation of metal hydrides at lower temperatures and hydrogen pressures.[39]

Lanthanum-Nickel System

In a study[40] where the effects of 300 ppm-levels of oxygen, water vapor, and carbon monoxide were investigated, it was found that $LaNi_5$ is only transiently poisoned by oxygen and water vapor. After an initial partial loss of capacity in oxygen or water, $LaNi_5$ almost completely recovers and then exhibits substantial immunity. However, carbon monoxide appears to be more detrimental to hydrogen adsorption by $LaNi_5$, appearing to form a simple chemisorbed monolayer that leads to the formation of nickel carbonyl. This renders inactive the nickel atom sites at which catalytic dissociation of hydrogen occurs. These studies were carried out at 25°C, so elevated temperatures may lead to reduced poisoning by carbon monoxide.

DEB System

As a developer of the crystalline organic getter technology, Honeywell Federal Manufacturing & Technologies has developed considerable data on the poisoning of DEB. In order to develop a conceptual design for the HALPAK concept described in the next section, Westinghouse Hanford Co. asked Honeywell Federal to perform DEB inhibition testing.[41] To qualify the DEB getter for the environment in a typical radioactive transportation package involving high-activity radioactive liquid waste (HALW), two environments were simulated: (1) a vapor environment consisting of potential getter poisons, e.g., ammonia, nitrous oxide, and carbon monoxide, in a typical underground storage tank, and (2) the waste environment, consisting of a simulant nonradioactive synthetic liquid waste prepared from a hypothetical recipe representing a typical underground storage tank. Getter configurations included plain pellets or pellets sealed in polyolefin bags and a silicone rubber boot. As expected, the rate of hydrogen adsorption is slowed by the presence of liquid and bags which slows hydrogen diffusion through the liquid or the bag to the getter. The capacity of the getter, however, was not affected. Testing with gas mixtures that would be expected to be generated during transportation of radioactive liquid wastes indicated that only carbon monoxide would be of concern for this getter. When CO (1% by volume) was part of the gas atmosphere, achieving less than 0.1% remaining hydrogen would take from 2 to 10 times longer, i.e., CO does not appear to poison the catalyst. The slowest rate observed in the study was expected to be several times faster than the actual generation rate of both hydrogen and the carbon monoxide by this waste. Based on the test conclusions, the getter is not inhibited by the HALW or by the products associated with it, except for the rate reduction caused by the carbon monoxide.[41] The rate reduction will only slow down the reaction, not stop it. Thus, reaction kinetics determines reaction rates.

USE OF GETTERS IN PACKAGING

TRUPACT-II is at least one example of a transportation package that could use getters to control hydrogen pressure generation. In fact, the schematics for the TRUPACT-II show provisions for accommodating a getter (catalyst) in the upper and lower aluminum honeycomb spacer

assemblies of the inner containment vessel.[41] Formal incorporation of getters within the TRUPACT-II is currently being proposed. Since the Safety Analysis Reports (SARs) of the TRUPACT-II have undergone a number of reviews by the Nuclear Regulatory Commission (NRC), it was important to attempt to ascertain the types of questions that the NRC would have concerning the use of getters in a package. While an attempt has been made in this paper to address these issues in some fashion, each item will not be discussed specifically for each hydrogen getter at this time. The following list[42] shows the nature of the NRC's concerns regarding the use of getters in the TRUPACT-II or any other transportation packaging.

- *Capacity*: What is the getter's capacity relative to the potential total gas generated during one year?
- *Pressure*: What is the maximum normal operating pressure (MNOP) during one year? Is the getter's performance affected by pressure?
- *Poisons*: Are there any chemical constituents in the contents that could potentially poison the getter?
- *Reversibility*: Under what conditions will the getter release hydrogen, and could these conditions occur during transport?
- *Temperature*: What is the effective temperature range of the getter relative to the temperature conditions specified in 10CFR71 (-20°F to 100°F plus solar insulation)?
- *Humidity*: What is the effect of water vapor on the getter? Will frozen getter still work?
- *Location*: Does the location of the getter matter? Consider stratification of the gases.
- *Thermal*: Does the getter release/absorb heat? If so, is this factored into the thermal and structural analysis?

DEB has been fully characterized for use within dry weapon environments.[44] In addition, DEB has been characterized for use as a tritium getter.[45] There is however, limited experience in using Honywell-Kansas City Plant getter technology with certified packaging. Sandia National Laboratories has obtained a DOE certification for the AL-SX (H1616) tritium container.[46] This container supports the limited life exchange program for tritium bottles. In addition to the tritium gas reservoirs for nuclear weapons, the AL-SX (H1616) is used to transport the Savannah River Site Hydride Transport Vessel. The design of the H1616 container uses two o-rings to provide a leak-tight containment vessel. Since tritium can permeate an elastomer O-ring, this could lead to a violation of the tritium containment criteria of 10 CFR 71 if the O-rings become exposed to the tritium environment. The solution was to fill the area between the inner and outer o-rings with DEB getter. The DEB would react with all the hydrogen (tritium in this case) escaping through the first O-ring and not allow any to reach the second O-ring. In this application, the DEB is sealed in, protected by an O-ring from both the contents and the environment.[47] It is interesting to note that the certifying authority (DOE/Albuquerque) considers the tritium getter in the AL-SX/3 (H1616-2) to be a filter, thus requirements of 10 CFR 71.51(c) are not met. Accordingly, transportation in the AL-SX/3 (H1616-2) is only allowed by an offsite transportation authorization rather than a certificate.[48]

DEB getter has also been successfully used at Argonne National Laboratory/West to protect spent enriched uranium metal fuels from hydrogen and water corrosion. This application placed the DEB in direct contact with the dry fuel inside an O-ring sealed container.[41]

The TRUPACT-II SAR sets forth the wattage limits for transuranic mixed waste drums destined for the Waste Isolation Pilot Plant in New Mexico. These wattage limits are derived from estimates of the amount of hydrogen calculated to be generated by radiolysis during a 60-day shipping period. Personnel at Los Alamos National Laboratory (LANL)[49] are working on two approaches to increase the wattage limits in the TRUPACT-II. The first strategy, which will not be discussed in detail, relies on the matrix depletion phenomenon that greatly reduces the potential for hydrogen generation, the second involves the investigation of the use of hydrogen getters to actively remove hydrogen from the headspace of the waste drums and/or the TRUPACT-II. LANL has been actively investigating the use of DEB as a possible hydrogen getter in TRUPACT-II. Their testing program includes the effects of inorganic gases, halogenated hydrocarbons, alcohols, ketones, and aromatics on the performance of DEB. Preliminary results from the testing program showed[50] that acetone, toluene, and methanol have no effect on the effectiveness of the getter. Similar to the previous discussion for the HALPAK, carbon monoxide was observed to result in a reversible inhibition in the LANL flow system. Carbon tetrachloride, on the other hand, had a dramatic detrimental effect on the gettering reaction. Spectroscopic analyses of the DEB after exposure to chlorinated organics indicated that chlorinated organics were not reacting with DEB by forming Pd-Cl salts. Preliminary tests using Tedlar® as a filtering medium indicate that chlorinated hydrocarbons and carbon monoxide are preferentially filtered from the getter while hydrogen is passing through. The Tedlar® seems to reduce the rate of gettering as a result of some reduction in the hydrogen diffusion rate to the getter compared with the gettering rate.[50] These results suggest that protected DEB is a possible getter candidate for these plutonium-bearing materials.

Under contract from the operator of the Super-Phenex NERSA, GNB Gesellschaft für Nuklear-Behälter mbH has designated and fabricated casks of the Type CASTOR BARRE to hold irradiated absorber rods from the fast breeder reactor SPX-1.[25] This cask is one member of a large CASTOR family of casks for the transport and dry storage of spent nuclear fuel and other high level radioactive materials. This cask was developed in compliance with International Atomic Energy Agency (IAEA) Safety Series No. 6, the acceptance criteria of the interim storage site, and compatibility with the available handling installations. The absorber rods contain boron carbide enriched in B-10 as absorbing material. Under the influence of radiation, tritium can be formed. According to burn-up calculations, a CASTOR BARRE cask loaded with 12 absorber rods may have a maximum tritium inventory of 1.6E15 Bq. Under dry storage conditions, the boron carbide will be locally heated to high temperatures by the decay heat from the tantalum pellets that are incorporated in the absorber rods. It is therefore not possible to exclude the possibility that part of the tritium inventory will be released into the inner cavity of the cask as gaseous tritiated hydrogen (HT) during interim storage. The tritiated hydrogen released from the absorber rods could possibly permeate into the walls of the cask and may thus contaminate the bulk of the cast iron material. The technical solution to overcome these problems was based on the idea of removing any tritium from the atmosphere inside the cask by

oxidizing the released HT with an appropriate oxidizing agent, manganese dioxide. In a second step, the resulting tritiated water is removed by chemically binding it in a suitable drying agent, calcium oxide. Manganese compounds are much less likely to be poisoned by chemical species such as carbon monoxide. In fact, there are no known manganese-carbon monoxide complexes where manganese is in either the +2 or +4 oxidation state. Thus, this particular hydrogen mitigation material also appears to be a promising candidate for a plutonium transport package.

Remediation of inventories of high-activity radioactive liquid waste (HALW) requires transportation of Type B quantities of radioactive materials, possibly up to several hundred liters. The only currently certified packaging is limited to 4 liter (L) quantities of Type B radioactive liquid in the PAS-1 cask. Scoping studies by the Westinghouse Hanford Co. and preliminary designs have identified the feasibility of retrofitting an insert into existing casks, allowing the transport of up to 380 L of HALW. This approach was referred to as the HALPAK concept.[51,52] The primary containment vessel for the HALW incorporates a gas mitigation system that includes a catalytic recombiner and hydrogen getter.[52] A gas-permeable splash shield covering a thin palladium plate that would enable hydrogen to permeate the isolated getter environment was proposed. The overpacks or secondary containment vessel envisioned for the HALPAK were the NuPac 72-B and the General Electric GE-2000. However, while the conceptual design studies for the HALPAK showed considerable promise, the regulatory climate and the lack of a clear-cut need for such a package ultimately prevented the full development of this type of packaging.

Another example of transport packaging, which proposed the use of hydrogen mitigation devices, is the NuPac-125B.[53] The Certificate of Compliance (#9200) for this packaging describes the contents as by-product and special nuclear material in the form of irradiated fuel particles, partial fuel rods, partial assemblies, and core debris, including filter-aid materials. The cask was first developed for the massive stabilization and cleanup activities required after to the Three Mile Island Unit 2 loss-of-coolant accident.[54] The interesting aspect of this particular cask is that it has the capability to ship wet demineralizing systems. The cask further includes pressure relief devices such as burst diaphragms and microporous graphite filters on each vessel to prevent the uncontrolled long-term buildup of non-recombinable gas mixtures. In addition, the canisters that will contain the contents actually incorporate catalytic recombiners in their design. While catalytic recombiners are not hydrogen getters from a mechanistic perspective, the formation of surface metal hydrides is analogous to the function of hydrogen getters. This particular transportation cask thus appears to set a precedent for the use of pressure mitigating devices in transportation casks.

EFFECTS OF RADIATION ON GETTERS

The response of materials to bombardment with energetic particles, radiation or heavy particles, is known to be dependent on material parameters (e.g., structure, impurity concentrations, cohesive properties, etc.) and irradiation parameters (flux, fluence, irradiation temperature, irradiation atmosphere, ion mass, and energy, etc.). However, despite the large body of information that has been gathered, the different responses of different materials to irradiation still not understood in detail. In general, inorganic substances such as metals and oxides are more resistant to radiation than organic substances such as polymers. This stems from the fact

that the radiolysis of inorganic substances proceeds by defect formation which is energetically more difficult than the chemical-bond fragmentation produced by radiolysis of organic substances. Textbooks showing the radiation stability of various substances commonly reflect this stability order by indicating that plastics begin to be affected by gamma radiation doses in the range of 10^6 to 10^8 rad. For ceramics and metals this radiation dose level is in the range of 10^9 to 10^{12} rad. However, the stability order for plastics can be further subdivided depending on the specific structure of plastic and type involved. For example, polytetrafluoroethylene (PTFE) is affected by gamma radiation dose levels as low as 10^4 rad, while polystyrene is resistant to 10^8 rad.

With regards to the previously mentioned hydrogen getters, limited information is available in the open literature. The obvious reasons for this sparse availability of information concerning radiation effects are that hydrogen storage materials were not intended for nuclear applications. However, the palladium-on-alumina catalyst used as a recombiner in the NuPac-125B has been reported to have had the longest successful history in highly radioactive environments[55]. In the case of DEB, Allied-Signal Aerospace has reported that they have functionally demonstrated that DEB can withstand radiation levels as high as 1 Grad. In the case of the MnO_2-based getter, researchers at the Forschungszentrum Juelich in Germany have reported[56] that the material is radiolytically stable at gamma-doses of 1 Mrad.

COMPATIBILITY OF GETTERS WITH THE PACKAGING

Prior to a discussion of compatibility issues, it is worthwhile to examine what is meant by compatibility. This will be done based on requirements given in packaging and transportation regulations of radioactive materials, i.e., 10CFR71.43(d)[57]. The general standard that must be met specifies that the package must be made of materials and constructions that assure that there is no significant chemical or other reaction between packaging components and the packaging contents including possible reactions with that of water leaks into the package. Similar to the effects of radiation on getters, little information is available in the open literature for most of the getters discussed in this paper. Of all the previously described hydrogen getters, DEB has been most evaluated for compatibility with packaging materials. Its interaction with various chemical constituents was addressed in the section on getter poisons. Because DEB is a mixture of an organic compound with palladium metal on carbon, it is expected to be chemically inert with regards to metal containment vessels and thermal insulation materials. The effect of water on DEB will slow down the gettering action of the material but will not result in any chemical reaction with DEB. In general, therefore, no reactions are expected between packaging components and DEB or the plutonium-bearing material contents in the package. A similar statement could be made for the PNNL composite getter. The getters are either metals, metal oxides, or organic materials and experience no incompatibility with any packaging components. Compatibility concerns could be an issue if water leaks into the package. As previously mentioned, the submersion of the DEB getter in water will dramatically decrease the ability of the getter to absorb gaseous hydrogen since the gettering reaction would be extremely diffusion limited. Reaction between the getter components and water is limited to reactive materials such as alkali metals and their oxides. From this reactivity perspective, the COMBOGETTER™ has

the greatest disadvantage since it contains an alkali-metal alloy ($BaLi_4$) and calcium oxide. Both of these materials react with water, evolving heat in the process. In the case of the alkali-metal alloy, the chemical reaction with water will evolve hydrogen gas. However, since the active getter and alkali-metal alloy are encapsulated by the calcium oxide, the reaction with water may be significantly reduced. Experimental work will be needed to evaluate the magnitude of these reactions. A possible solution to these reactions is the further encapsulation of the getter that will limit the access of free water to the getter.

REGULATORY PRECEDENTS

In the NRC has not approved using hydrogen getters in packaging.[58] Thus, no regulatory precedents for the use of getters in the U.S. currently exist. However, according to the NRC[58] they have reviewed several applications proposing the use of getters. The strength of the technical arguments made in the application for a package will determine whether regulatory acceptance is forthcoming. It would appear that, if the NRC's concerns outlined in the previous section could be adequately addressed in the packaging application, regulatory acceptance of getters or recombiners might be attained.

DESIGN CONSIDERATIONS

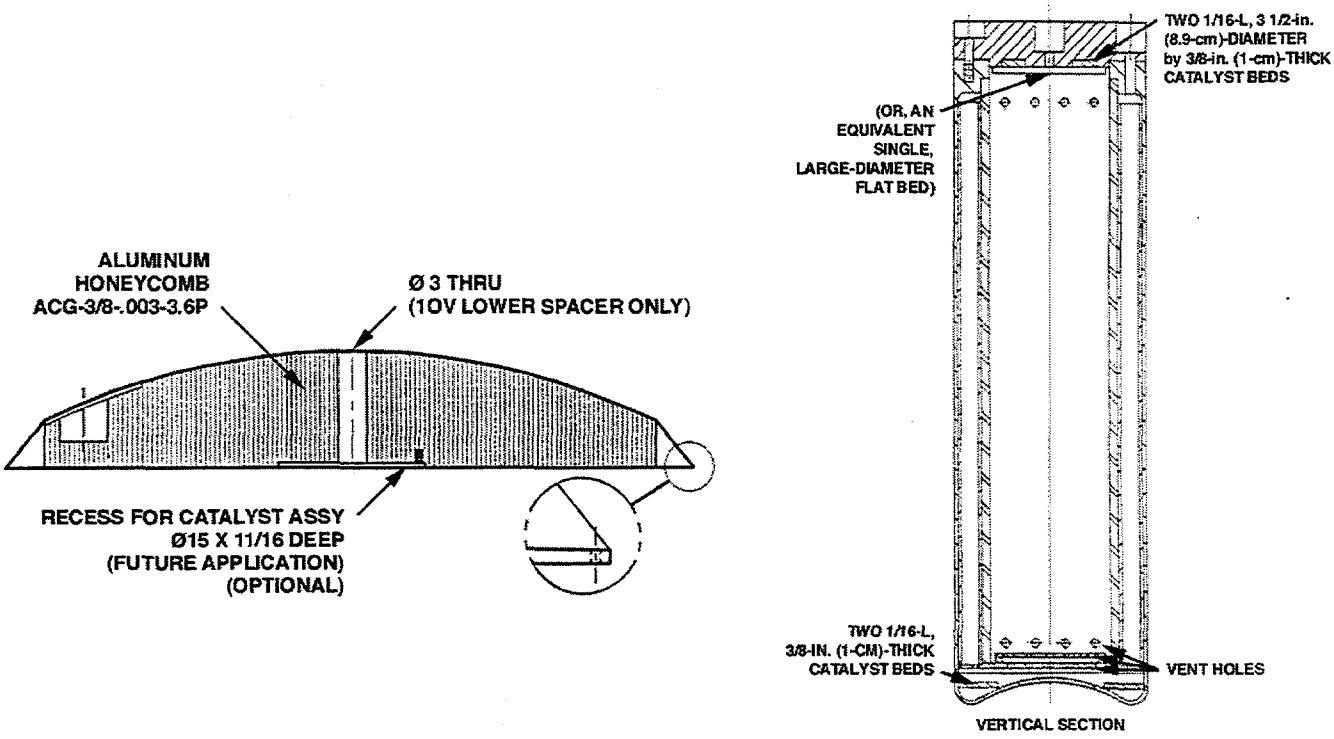
When the hydrogen getter is able to remove hydrogen-oxygen gases in a stoichiometric 2-to-1 ratio by forming water, the getter is referred to as a recombiner, and provides a dual role. Materials in this category are precious metal such as palladium on solid supports like alumina. When nonstoichiometric net gas generation occurs, such as in cases where oxygen is being scavenged by the contents, hydrogen can build up in excess. If the oxygen is sufficiently limited, there is little hazard from a flammability standpoint; however, excess hydrogen can cause over-pressurization of the container and provides a potential for ignition if the container vents to the atmosphere or if air leaks into the container. To prevent the potential occurrence of such events, certain design features must be considered in the packaging. Among the issues that need to be considered for the incorporation of getters into a transportation package are getter bed design, getter bed fabrication, and getter bed location, and getter bed. These issues will be discussed below.

When wet conditions are expected, the getter must be one that will not react with water. A mixture of silicone-coated palladium catalysts, such as those developed by Atomic Energy of Canada Limited, have been found useful under very wet conditions.[54] Since such conditions are not expected for the plutonium-bearing waste materials considered for transportation here, a large selection of getters is available.

The size and shape of the getter bed is related to the container design. Highly effective getter bed designs are thin (approximately 1-cm thick) disk-shaped beds. When the getter is in the form of pellets, the getter bed is typically contained by a wire screen. Heavy wire (8-mesh) construction affords maximum bed protection and a large, effective open area for gas diffusion.

The getter bed location is an important design consideration since it could affect the performance of the getter. In the TRUPACT-II and the NuPac-125B, the getter beds were placed into both

ends of the container. The locations are shown in Figure 1. It should be noted that in the TRUPACT-II and the NuPac-125B the hydrogen getters are referred to as catalysts and recombiners, respectively. While stratification of hydrogen is not expected in either package, the designers have relied on a symmetrical placement to avoid this problem should it occur. For the NuPac-125B, the possibility that a submerged getter bed could be produced by the wet contents of the canister necessitated the use of top and bottom beds in this particular design. Where water is totally absent, a single bed near the top of the container or the primary containment vessel is adequate. Other getter bed locations could be used depending on the package design requirements.



(a) (b)

Figure 1. Location of Getter in TRUPACT-II (a) and NuPac-125B (b). Note that getters are referred to as catalyst and recombiner in these packages.

Specific design features for getter assemblies will depend on the physical form of the contents, the size, design and porting of the container, and the intended purpose (i.e., storage or transportation). However, the getter assembly located in a container of radioactive material for gas control should meet the following criteria:

- The getter bed must be exposed to the gas/vapor space at all times.
- The amount of exposed getter required is proportional to the gas generation rate. The recommended ratio of bulk volume of the getter to the gas generation rate, in mL of getter per mL of hydrogen and oxygen gas produced per hour, is 1.0. Thus, a generation rate of 50 mL/h requires a 50-mL bed of getter.
- The recommended ratio of getter bed volume in mL to exposed surface area in cm^2 is 1.0.[55]

Testing of the getter should be performed using a gas flow rate that is three times higher than those used to establish the size of the getter bed. Tests should also be conducted at temperatures below freezing to show that the getter beds, as designed, would remove gases at the design rate for at least a few weeks under low temperature conditions.

CONCLUSIONS AND RECOMMENDATION

NRC concerns include getter capacity, pressure effects, poisons, reversibility, temperature, humidity, location, and thermal effects on getter performance within the packaging. These concerns in general point to a choice for appropriate getters from the irreversible class of getter materials. Specifically, the getters that rely on the reduction of a metal oxide appear to offer certain advantages. The getter chemistry of manganese oxides and cobalt oxides suggests minimal impact by pressure, poisons, reversibility, temperature, and thermal effects. Additionally, these getters contain drying agents that will chemically combine with water vapor, thereby removing this component from the packaging environment. The commercial cobalt oxide getter COMBOGETTER™ is available from SAES and appears to satisfy many of NRC's concerns. However, the fact that this material, in addition to gettering potential poisons such as carbon oxides, hydrogen halides, hydrogen sulfides, will also getter the nitrogen and oxygen found in the air could pose problems. This gettering action might result in the evacuation of the primary container in the transportation packaging. In the case of the 9965-9975 family of packages,[59] the cone closure lids may be difficult to remove if less than ambient pressures exist in the containment vessel.

To address the question of vacuum production in the presence of the contents being contemplated in the 9965-9975 packages, some preliminary testing will need to be performed to fully explore the feasibility of using materials such as either the manganese oxide or cobalt oxide system. The well-known organic hydrogen getters based on DEB or similar systems are another class of candidate getters for the 9965-9975 packages. The relatively clean nature of the proposed contents in these packages in relation to potential gas generation also suggests consideration of organic hydrogen getters. The ability to form composites of DEB getters with silicone rubber or other encapsulants could lead to selective removal of hydrogen thereby significantly reducing the potential deflagration risk. Researchers at PNNL recently developed a

two-piece zirconium-based getter described as PNNL composite. The attractive feature of this getter is a coating that provides a protective barrier against gases that could poison the getter but that permits the transport of hydrogen to the getter surface. More important, this feature of the getter appears to allow its use at ambient temperature in air. A preliminary comparison of the PNNL Composite, DEB or similar polymer-based getters, manganese dioxide-based getters, and the COMBOGETTER™ is made in Table 1.

Table 1. Performance Comparisons for PNNL Composite, DEB, MnO_2, and COMBOGETTER™

Regulatory Concern	PNNL Composite	DEB	MnO_2/Ag_2O	COMBOGETTER(TM)
Capacity (during 1 yr)	160 cc-atm/g	243 cc-atm/g	200 cc-atm/g	109 cc-atm/g
Pressure (performance effects)	1/2 order dependence	Unknown	Unknown	Unknown
Poisons (contents)	Unaffected (?)	Effects rate	Unaffected (?)	Unaffected (?)
Reversibility (release hydrogen)	Reversible at >500°C	Irreversible	Irreversible	Irreversible
Temperature (effective range)	Unknown	-65 to 175 F	Unknown	Unknown (< 300 F)
Humidity (frozen getter)	Unaffected (?)	slower	Unknown	Unaffected (?)
Location (stratification)	Yes	Yes	Yes	Yes
Thermal (heat release)	exothermic	exothermic	Unknown	Unknown

The basis for this comparison is NRC concern about getter usage in packaging. This preliminary comparison was made based on data currently available from the literature (see Bibliography). Further data may be contained in the safety analysis reports of specific packagings where getter usage is envisioned, e.g., latest SARP revisions of TRUPACT-II, etc. Nevertheless, from the currently available literature, the gettering features of each getter were tabulated. Since answers to a number of regulatory concerns are currently unknown, it is not possible to identify the best hydrogen getter candidate from this set of getters. Testing, or evaluation of existing test data, may enable the identification of a superior getter type. At this time, the PNNL composite getter, DEB or similar polymer-based getters, the MnO_2 system, and the COMBOGETTER™ appear to be attractive candidates to help reduce pressurization from radiolytic reactions in transportation packaging. If capacity and proven utilization in nuclear material packages are chosen as selection criterion, then DEB or similar polymer-based getters and MnO_2 appear to be reasonable materials for further investigation.

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Ajayan, P. M. and T. W. Ebbesen (1997). "Nanometre-size tubes of carbon." *Rep. Prog. Phys.* **60**: 1025-1062.

This paper reviews the present state of understanding of the structure, growth, and properties of nanometer-size tubes of carbon.

Bagdanovic, B. (1984). "Magnesium Hydride: A Homogeneous-Catalyzed Synthesis and Its Use in Hydrogen Storage." *Int. J. Hydrogen Energy.* **9**(11): 937-941.

A short review of the use of hydrogen as an energy source, and problems associated with hydrogen storage is followed by a discussion of the preparation and properties of magnesium hydride.

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Bennett, L. G. I., S. D. Argunder, et al. (1986). "Investigation of Hydriding Processes in Low-Temperature/Low-Pressure Metal hydrides." *Int. J. Hydrogen Energy.* **11**(9): 577-582.

The properties of certain metal hydrides with equilibrium pressures of 1-2 MPa in the temperature range from 80 to 100°C were investigated for their applicability to special temperature-sensitive devices incorporated into a process system for control and safety functions.

Boffito, C., B. Ferrario, et al. (1981). "A Nonevaporable Low temperature Activatable Getter Material." *J. Vac. Sci. Technol.* **18**(3): 1117-1120.

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This paper describes the major design issues for packaging and transportation of plutonium contaminated wastes with regard to gas generation.

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della Porta, P. (1996). "Gas Problem and Gettering in Sealed-Off Vacuum Devices." *Vacuum.* **47**(6-8): 771-777.

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Devillers, M., M. Sirch, et al. (1990). "Characterization of the ZrCo-Hydrogen System in View of Its Use for Tritium Storage." *Chem. Mater.* **2**: 255-262.

This paper reports on measurements of the absorption and desorption isotherms of hydrogen and deuterium using a volumetric technique.

Devillers, M., M. Sirch, et al. (1992). "Hydrogen-Induced Disproportionation of the Intermetallic Compound ZrCo." *Chem. Mater.* **4**: 631-639.

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Garg, S. P., E. A. Gulbransen, et al. (1990). "Zr Powder and Zr-16% Al Alloy as Getters for O_2, H_2, H_2O, CO and CO_2 Gases." *Vacuum.* **40**(3): 275-280.

The capacity and reactivity of zirconium powder and St 101 pellets were studied using a sensitive vacuum microbalance, a mass spectrometer, and Debye-Scherrer X-ray diffraction.

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Gilliom, L. A. (1988). "A New Polymer-Based Hydrogen Getter." *Material Research Society Symposium Proceedings.*

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Gilliom, L. R. (1989). "Catalytic Hydrogenation of Polymers in the Bulk." *Macromolecules.* **22**: 662.

This paper describes the bulk hydrogenation of polymers.

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This paper discusses bulk hydrogenation of polymers

Giorgi, E., C. Boffito, et al. (1990). "A New Ti-Based Non-Evaporable Getter." *Vacuum.* **41**(7-9): 1935-1937.

This paper presents the properties of a new titanium-based gettering material that has been found to have the high porosity for efficient room temperature sorption combined with mechanical strength.

Giorgi, T. A. (1974). "Getters and Gettering." *Japan J. Appl. Phys.* **2**(1): 53-60.

The principal modern getter devices characteristic of each of the two main getter families, i.e., flash and bulk are established and briefly illustrated.

Giorgi, T. A., B. Ferrario, et al. (1985). "An Update Review of Getters and Gettering." *J. Vac. Sci. Technol.* A **3**(2): 417-423.

A brief review of present day getter materials is made with reference to the two principal families, i.e., evaporable and nonevaporable materials.

Havens, S., C. C. Yu, et al. (1981). "Improved Syntheses of Benzils as Polymer Intermediates." *J. Poly. Sci.: Poly. Chem. Ed.* **19**: 1349-1356.

This paper describes methods of synthesis of benzils and some new combinations of old reactions developed to make these materials more readily available as polymer intermediates.

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A tritium transport vessel using depleted uranium was tested in the laboratory using deuterium and hydrogen.

Holtz, R. L., V. Provenzano, et al. (1996). "Overview of Nanophase Metals and Alloys for Gas Sensors, Getters, and Hydrogen Storage." Nanostructured Materials. **7**(1/2): 259-264.

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This paper describes the use of the above diacetylene compound for gettering hydrogen. The aging of HCPB at 70°C in nitrogen is reported.

Konishi, S., H. Yoshida, et al. (1985). "Experiments on Ceramic Electrolysis Cell and Palladium Diffuser at the Tritium Systems Test Assembly." Fusion Technology. **8**(September): 2042-2047.

This paper describes a fuel clean-up system.

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In this paper the authors report the preparation of monocrystalline Mg and Mg_2Ni by mechanical alloying and investigate their thermal stability and hydrogen storage properties.

Manani, P. (1997). "The COMBOGETTER(TM) as a Key Component in the Vacuum Insulation Panels (VIPs) Technology." Vuoto. **XXVI**(2): 45-53.

This novel gettering system, which is able to efficiently chemically absorb a wide range of gases, and its role as an integral component in VIPs are discussed.

Manchester, F. D. and D. Khatamian (1988). "Mechanisms for Activation of Intermetallic Hydrogen Absorbers." *Hydrogen Storage Materials*. R. G. Barnes. Aedermannsdorf, Switzerland, Trans Tech Publications. **1:** 261-296.

This section provides an overview of mechanisms of activation in intermetallic hydrogen absorbers.

Maynard, K. J., W. T. Shmayda, et al. (1995). "Tritium Aging Effects in Zirconium-Cobalt." *Fusion Technology*. **28**(October): 1391-1397.

The effects of tritium aging on ZrCo have been characterized to determine the suitability of ZrCo as a long-term tritium storage medium.

Miller, H. H., E. R. Bissell, et al. (1981). "Tritium Gettering by Acetylenes in Static Air." *J. Nucl. Materials*. **101**: 238-239.

The paper reports that acetylenes do react with tritium in the presence of large quantities of oxygen. The data suggests effective gettering for 0.1 to >1% tritium-in-air mixtures.

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Murphy, D. W., S. M. Zahurak, et al. (1993). "A New Route to Metal Hydrides." *Chem. Mater.* **5**: 767-769.

This paper reports on the use of borohydrides in aqueous solution as a convenient reagent to produce metal hydrides.

Nemirovskaya, I. E., V. Z. Mordkovich, et al. (1992). "Hydrogen Sorption in $LaNi_{4.98}$ $Al_{0.02}$-H_2 at Low Temperatures." *Thermochimica Acta.* **194**: 253-258.

This paper investigated the above system under atmospheres of hydrogen and inert gas by differential scanning calorimetry in the temperatures range 240 to 260°K.

Nohara, S., N. Fujita, et al. (1998). "Electrochemical Characteristics of a Homogeneous Amorphous Alloy Prepared by Ball-Milling Mg_2Ni with Ni." *J. of Alloys and Compounds.* **267**: 76-78.

In this work, a homogeneous amorphous alloy was prepared by ball-milling Mg_2Ni with Ni under the different conditions from those used by Kohno et. al. and the electrochemical characteristics of the alloy were investigated.

Orimo, S., H. Fujii, et al. (1994). "Synthesis of Fine Composite particles for Hydrogen Storage, Starting from Mg-YNi_2 Mixture." *J. of Alloys and Compounds.* **210**: 37-43.

New composite particles were synthesized for hydrogen storage on the basis of an idea for particle design.

Pederson, A. S. and B. Larsen (1993). "The Storage of Industrially Pure Hydrogen in Magnesium." *Int. J. Hydrogen Energy.* **18**(4): 297-300.

The effects of impurities on the hydrogen storage capacity of Mg was studied.

Penzhorn, R.D., U. Berndt, et al. (1997). "Performance Test of Palladium/Silver Permeators With Tritium at the Tritium Laboratory Karlsruhe." *Fusion Technology.* **32**(September): 232-245.

The permeation of hydrogen, deuterium, and tritium through Pd-Ag permeators of different configurations were compared. The poisoning of Pd-Ag by methane and other hydrocarbons is slow at 360°C.

Penzhorn, R.D., M. Deviellers, et al. (1991). "Storage of Tritium in ZrCo Alloy: Effect of Pre-Exposure to Impurities Relevant to the Fusion Cycle." *J. Nucl. Mater.* **179-181**: 863-866.

To evaluate ZrCo as a getter material for storage, transport, and handling of tritium a study of the effects of N_2, O_2, CO, CO_2, methane, and ethane on the pressure-composition isotherms, storage capacity and reaction rate of $ZrCo/H_2$ system was carried out.

Penzhorn, R.D., M. Sirch, et al. (1995). "Hydrogen Sorption Rate by Intermetallic Compounds Suitable for Tritium Storage." *Fusion Technology.* **28**(October): 1399-1403.

The kinetics of the sorption of molecular hydrogen by the above two materials were investigated as a function of temperature at several constant pressures of hydrogen.

Perevezentsev, A. N., A. C. Bell, et al. (1995). "Safety Aspects of Tritium Storage in Metal Hydride Forms." *Fusion Technology.* **28**: 1404-1409.

Air or nitrogen ingress accident scenarios into tritium storage containers filled with uranium or intermetallic compound hydrides are discussed based on the experimentally determined kinetics of the reaction of these hydrides with air, oxygen and nitrogen.

Post, M. L., J. J. Murray, et al. (1984). "Metal Hydride Studies at the National Research Council of Canada." *Int. J. Hydrogen Energy.* **9**(1/2): 137-145.

The paper describes reaction of gaseous hydrogen with binary intermetallics $LaNi_5$, $CaNi_5$, and Mg_2Ni. Calorimetry was used to determine enthalpic behavior.

Reilly, J. J. and G. D. Sandock (1980). "Hydrogen Storage in Metal Hydrides." *Sci. Amer.* **242**(February): 118-129.

The exploitation of hydrogen as a fuel for motor vehicles requires a method for storing it safely and compactly at ambient temperature. Forming metal hydrides by forcing it into the gaps among metal atoms may be the best approach.

Reilly, J. J. and R. H. Wiswall (1968). "The Reaction of Hydrogen with Alloys of Magnesium and Nickel and the Formation of Mg_2NiH_4." *Inorg. Chem.* 7(11): 2254-2256.

Mg_2Ni readily reacts with hydrogen at 300 psia and 325°C.

Riley, D. L., J. C. McCoy, et al. (1996). "Hydrogen Gettering the Overpressure Gas from Highly Radioactive Liquids." Transport and Storage of Radioactive Materials, ASME.

This paper describes concepts for the mitigation of gas generation in a proposed transport package for 4 L quantities of high-activity radioactive liquids.

Riley, D. L., J. R. Schicker, et al. (1995). "Hydrogen Gas Control Inside Anaerobic Transport Packaging." *PATRAM'95*, Las Vegas, NV.

This paper describes the issue of hydrogen gas generation and its control in transport packages.

Robinson, S. L. and J. L. Handrock (1994). *Hydrogen Storage for Vehicular Applications: Technology Status and Key Development Areas*, SAND94-8229, Sandia National Laboratories.

The state-of-the-art of hydrogen storage technology is reviewed, including gaseous, liquid, hydride, surface adsorbed media, glass microspheres, chemical reaction, and liquid chemical technologies.

Rodrigo, L., J. A. Saweicki, et al. (1995). "Characterization of Deactivated Metal Getters Used in a Glovebox Purification System." *Fusion Technology.* **28**(Oct.): 1410-1415.

A postmortem analysis of samples of deactivated SAES St707 getter particles recovered from a glovebox purification system was conducted to determine the cause of the deactivation and hydrogen capacity loss.

Sandrock, G. D. and P. D. Goodell (1980). "Surface Poisoning of $LaNi_5$, FeTi, and (Fe, Mn)Ti by O_2, CO, and H_20." *J. Less-Common Metals.* **73**: 161-168.

This paper is a brief summary of an extensive experimental program performed to understand the surface poisoning of metal hydrides by impurities in the hydrogen used.

Sano, M., H. Nishimura, et al. (1989). "Dissociation of Hydrogen Molecules by First-Stage Graphite-Cesium Intercalation Compounds." *Syn. Metals.* **31**: 73-78.

A cesium intercalation compound was found to dissociate hydrogen molecules on its surface using a hydrogen-deuterium equilibration reaction.

Selvam, P., B. Viswanathan, et al. (1986). "Magnesium and Magnesium Alloy Hydrides." *Int. J. Hydrogen Energy.* **11**(3): 169-192.

This review addresses the question of using magnesium and magnesium-based alloys as "rechargeable hydrogen storage" media.

Shaltiel, D., I. Jacob, et al. (1977). "Hydrogen Absorption and Desorption Properties of AB2 Laves-Phase Pseudobinary Compounds." *J. Less-Common Metals.* **53**: 117-131.

The formation and properties of the hydrides of the pseudobinary intermetallic compounds were studied at various temperatures and at pressures up to 70 atm.

Shepodd, T. J. and B. L. Phillip (1997). Materials for the scavanging of hydrogen at high temperatures. US 5,703,378.

This patent describes a hydrogen getter composition comprising a double or triple bonded hydrocarbon with high melting point useful for removing hydrogen gas to partial pressures below 0.01 torr from enclosed spaces and particularly from vessels used for transporting or containing fluids at elevated temperatures.

Shepodd, T. J. and B. L. Phillip (1997). Materials for the scavanging of hydrogen at high temperatures. US 5,624,598.

This patent describes a hydrogen getter composition comprising a double or triple bonded hydrocarbon with a high melting point useful for removing hydrogen gas to partial pressures below 0.01 torr from enclosed spaces and particularly from vessels used for transporting or containing fluids at elevated temperatures.

Shepodd, T. J. and H. M. Smith (1990). "Hydrogen-Tritium Getters and Their Application," Allied-Signal Aerospace Corp.

This paper describes the properties of DEB. It mentions the use of compression-molded DEB-polyethylene composite, DEB-filled urethane adhesive, and DEB-filled castable RTV silicone.

Shepodd, T. J. and L. L. Whinnery (1998). Polymer formulations for gettering hydrogen. US 5,837, 158.

This patent describes a novel composition comprising organic polymer molecules having carbon-carbon double bonds for removing hydrogen from the atmosphere within enclosed spaces.

Shores, A. A. (1991). "An Effective Moisture Getter Coating for Hermetic Packages." 5th Int. SAMPE Electronics Conference, Los Angeles.

This paper reports experimental data on the enormous moisture gettering capacity of a new coating composition at various temperatures at equilibrium with a wide range of water vapor concentrations.

Shores, A. A. and R. Miculich (1992). "Effective Gettering Materials for Hermetic Packages." ISHM '92, San Fransisco, Int. Soc. Hybrid Microelectronics.

This paper reports on the various gettering compounds: particle getters, moisture getters, and particle and moisture getters.

Skerrett, P. J. (1993). "Solid Progress in Hydrogen Storage." *Technology Review*. (February/March): 15-16.

This article discusses storing hydrogen as a solid in combination with other materials and then liberating the gas on demand through chemical reaction.

Smith, H. M., T. J. Shepodd, et al. (1980). "Organic Getter Materials for the Removal of Hydrogen and Its Isotopes, " Allied-Signal Aerospace Co.

This paper describes a hydrogen getter technology developed at SNL and KCP over the past decade.

Song, M. Y. and H. R. Park (1997). "Verification of the Rate-Controlling Step in the Dehydriding Reaction of Mg_2Ni hydride." *J. Mater. Sci. Letters*. **16**: 1774-1775.

This paper indicates that the rate-controlling step in the dehydriding reaction of Mg_2Ni is the mass transport of hydrogen molecules through pores, interparticle channel of cracks.

Song, M. Y. and H. R. Park (1998). "Pressure-Composition Isotherms in the Mg_2Ni-H_2 $_s$System."
J. Alloys and Compounds. **270**: 164-167.

Preparation and absorption and desorption isotherms were obtained. Relationships for equilibrium pressures for adsorption and desorption were given.

Souers, P. C., E. R. Bissell, et al. (1982). "Organic Getter for Tritium." *J. Vac. Sci. Technol.* **20**(4): 1132-1134.

This paper reports the gettering of ppm-level tritium by acetylenes and observes that the acetylenes failed to satisfactorily getter tritium at 1 ppm.

Srivastava, S. and O. N. Srivastava (1999). "Synthesis, Characterization and Hydrogenation Behavior of Composite Hydrogen Storage Alloys, $LaNi_5/La_2Ni_7$, $LaNi_3$." *J. Alloys and Compounds*. **281**: 197-205.

The present investigation examines the above composite hydrogen storage materials for use with efficient, high energy density Ni-Metal Hydride batteries

Tamm, U., E. Hutter, et al. (1992). "Uranium Getters for Tritium Cleanup at the Tritium Laboratory Karlsruhe (TLK)." *Fusion Technology*. **21**(March): 983-987.

In a three-stage tritium cleanup system the gaseous impurities oxygen, nitrogen, carbon dioxide, methane, ammonia, and water are removed from a contaminated hydrogen stream.

Trujillo, R. E. and R. L. Courtney (1977). "Organic hydrogen getters Part 2. Hydrogen rates of solid alkynes on palladium-calcium carbonate catalysts." *J. Mater. Sci.* **12**: 937.

This paper describes reaction rates for the hydrogenation of 27 acetylenic materials, both compounds and polymers.

Tsuchiya, K., H. Imaizumi, et al. (1995). "Preliminary Characterization of Zr_9Ni_{11} Alloy for Its Tritium Gettering Property in In Situ Irradiation Test." *Fusion Technology*. **28**(October): 1431-1436.

The evaluation of the getter materials examined leads to the conclusion that the Zr_9Ni_{11} alloy may be used for the in situ irradiation test of a fusion blanket.

Wang, Q. and J. K. Johnson (1999). "Molecular Simulation of Hydrogen Adsorption in Single-Walled Carbon Nanotubes and Idealized Carbon Slit Pores." *J. Chem. Phys.* **110**(1): 577-586.

Ambient temperature isotherms indicate that an array of nanotubes is not a suitable sorbent material to achieve DOE targets for vehicular hydrogen storage.

Woyke, T., C. Schiller, et al. (1995). "ZrCo as a New H_2 Storage and Getter for Lyman-Alpha Radiation sources." *Appl. Optics.* **34**(1): 155-157.

Using ZrCo, radiation sources with a large Lyman-α radiation output and high spectral purity were produced and successfully applied in a Lyman-α fluorescence hygrometer for stratospheric observations.

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