Hydrogen Gas Control Inside Anaerobic Transport Packaging[*]

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BACKGROUND ON RADIOACTIVE LIQUID WASTE GENERATION AND STORAGE

Former defense production and waste processing has produced approximately 353,000 m^3 of complex radioactive waste. The majority of this waste is currently being stored in underground storage tanks (UST) at two locations, the Hanford Site, and the Savannah River Site (Cruse et al. 1992). The current plan for the remediation of these wastes involves characterization, pretreatment and bench scale testing (Straalund et al. 1992, Morford and Bridges 1993, and Barker et al. 1993). All three of these remediation processes require that the waste be transported, and in some cases, this involves off-site shipment of type-B quantities of radioactive liquid waste.

STATUS AND REVIEW OF RADIOACTIVE LIQUID TRANSPORTATION

The United States Department of Energy and the Nuclear Regulatory Commission (DOE, NRC) currently have no packages certified specifically for shipment of type-B quantities of radioactive liquid waste. The largest quantity of type-B liquid waste that can be transported is 50 ml (0.01 gal), using a PAS-1 package (Nuclear Packaging 1989). However, Westinghouse Hanford Company (WHC) is currently in the process of obtaining an amendment to the license of the PAS-1 cask (VECTRA 1995), allowing the transport of up to 4 liters (1.1 gal) of radioactive type-B liquid to off-site laboratories for analysis. The PAS-1 Cask will primarily be used by the Hanford site Tank Farm Characterization and Laboratory organizations to ship radioactive waste tank samples to offsite labs, including the Idaho National Engineering Laboratories (INEL) and Los Alamos National Laboratories (LANL). The payload will consist of Type B quantities of tank samples, consisting of liquids and sludges of mixed fission products (primarily Cs^{137} and Sr^{90}).

Internationally, bulk-quantities of radioactive liquid shipments have been transported for many years. For example, between 1956 and 1962, the Commissariate A L'Energie Atomiqe developed and use-tested 38 models of standardized liquid packaging (the "Cendrillon" cask family). By 1974, 188 packages were licensed by the International Atomic Energy Agency (IAEA) and in use for long distance transfer of 3 L (0.8 gal) to 200 L (53 gal) of highly radioactive liquids in Europe (WHC 1993). The Germans have

recently carried out a bulk-quantity radioactive liquid transport campaign. The intent is to remove high active liquid waste (HAWC) from Karlsrhe Reprocessing Plant to the Pamela vitrification facility in Dessel/Belgium. The GNB has developed the CASTOR V/HAWC, with a capacity of 3,500 L (915 gal) (Fleisch et al. 1994 and Spilker et al. 1994). Like the Germans, France also needed larger transport packaging. Three packagings, the LR-54 -56 and -44, all larger then the largest Cendrillon cask, were developed. These large French casks range in capacity from 1,280 L (340 gal) to 19,500 L (5,100 gal). As there are no equivalent packages in the United States and only brief developmental work has been conducted by the DOE (WHC 1993, and Riley et al. 1994), one of these transporters, the LR-56, has been procured for on-site transfers of liquids for the Hanford site. The LR-56/H Cask System fabrication is complete, and the unit is currently enroute to Hanford. An onsite SARP is complete and in review (WHC 1995).

GAS GENERATION INSIDE USTS

As a result of radiolysis, thermolysis, and organic and chemical activity, the radioactive wastes produce a variety of gases. For example, the well known (formerly "burping") Hanford Tank 101–SY, produces approximately 30–35% H_2, 25–30% N_2O, 20–25% N_2, 12–18% NH_3, and less than 1% CH_4 (Babad et al. 1992 and McDuffie 1994). Most gases do not pose a problem for packaging safety; however, hydrogen and nitrous oxide, when combined in quantities exceeding their lower flammability limit, can deflagrate. A hydrogen/nitrous oxide deflagration, depending on the concentrations, can typically exceed a factor of ten increase in pressure. For stoichiometric mixtures of hydrogen and nitrous oxide, it is possible to achieve a detonation (Cashdollar et al. 1992). For these reasons, in 1984 the NRC released Information Notice No. 84–72: *Clarification of conditions for waste shipments subject to hydrogen gas generation* (NRC 1984). The notice outlines the method to assure that hydrogen generated as gas will not exceed 5% by volume and that any portion of a package (secondary container) exposed to hydrogen will have a 5% by volume oxygen limit.

Given the fact that radioactive wastes produce gas, and that NRC licensed packagings cannot be vented, several possible methods exist to overcome the hydrogen-accumulation problem (Henrie et al. 1986). These include 1) limiting the shipping time, therefore not allowing the generated gases to exceed the lower flammability limit, 2) reducing the amount of waste per package volume, thus providing a large void space, or 3) providing gas mitigation, permanently or temporarily canceling the gas generation.

It is often not possible to accurately determine the species and concentrations of gases being generated from a particular waste (Hobbs et al. 1992). Estimates and measurements can be made for some wastes that will allow acceptable shipping windows, thus reducing the amount of time that the gases are allowed to generate (Flahery et al. and WHC 1993). Also, some shipping requirements allow or justify transporting a relatively small quantity of waste in a relatively large transporter, thus providing a void space large enough to extend shipping times. There are, however, several cases where it is desirable to ship larger quantities of materials in a smaller package. Two examples that have been developed recently, are the Type–B Drum Overpak, a container designed to overpak a standard 55-gallon TRU waste drum, in the smallest possible volume (Edwards 1995), and HALPAK, the bulk-quantity high-activity type-B liquid package (Meinert et al. 1994 and Riley et al. 1994).

The moment that a radioactive liquid package is sealed, the gases begin to concentrate, and potentially flammable concentrations must be accounted for, both from a licensing and safety (operations) point of view. Providing a package with a gas-mitigation system will produce a safer package and will yield several benefits.

SOLUTIONS TO HYDROGEN ACCUMULATION

Passive gas mitigation systems, i.e., hydrogen recombiners, have been used for many years and are very effective at combining hydrogen with oxides (Henrie et al. 1986, Nuclear Packaging 1991). Their only shortcoming is the requirement that an oxide be present. In a sealed package containing a gas producing waste and hydrogen recombiners, the hydrogen will combine with oxides until either the hydrogen or oxide is consumed. Hydrogen is typically produced more abundantly than oxides in radioactive waste. This unbalance causes the oxide to be consumed and hydrogen will continue to accumulate. Although no oxide will be present to allow a deflagration to initiate, a safety problem exists. It is generally assumed that a radioactive hydrogen pressure vessel should be avoided, and in fact, is the NRC's intent with Notice No. 84–72.

A solution to the hydrogen accumulation in the absence of oxides can be accomplished by using getters. Getters, specifically, crystalline getters (Courtney and Harrah 1977), will irreversibly remove hydrogen by catalytic hydrogenation of unsaturated organic compounds without the need or existence of oxides.

The AlliedSignal Aerospace Co. Kansas City Division (AS–KCD) has had extensive experience in crystalline organic getter technology since 1978 developing organic hydrogen getters for the DOE Nuclear Weapons Complex (Smith 1987). The compound DEB; 1,4-bis(phenylethynyl)benzene (Havens et al. 1981) is the fourth generation of getter development and is the standard DOE production hydrogen getter material. DEB has been fully characterized for use inside dry weapon environments (Tinnel and Leckey 1989). In addition, DEB has been characterized for use as a tritium getter (Shepodd et al. 1990). There is however, limited experience in using AS-KCD getter technology with licensed packaging. Sandia National Laboratories, Albuquerque, has obtained a DOE license for the H1616 tritium container. This container supports the limited life component exchange program for tritium bottles. The design of the H1616 container uses two O-rings to provide a leak-tight containment vessel. Tritium, however, can permeate an elastomer O-ring, and this could lead to a violation of the tritium containment criteria of 10 CFR 71 (NRC 1993), 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) permeating 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 (Gilliom et al. 1992).

DEB getter has also been successfully used, at Argonne National Laboratories/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.

However, for radioactive waste shipments requiring hydrogen control in the vapor space, the getter needs to be located in the containment vessel. (Note: WHC has filed an Invention Disclosure for an externally-located Gas Control Unit; however, information cannot be released at this time). This places the DEB getter in the presence of the gases and potentially in direct contact with the waste form, e.g., liquid. This contact, both with the liquid and vapor, has the potential to poison the effectiveness of the getter's ability to remove the hydrogen. As a result of this concern, the Transportation Management Division (TMD) of DOE/HQ asked AS–KCD to perform hydrogen-getter (DEB) inhibition testing (Schicker 1995).

To qualify the DEB getter for the environment in a typical radioactive transportation package, two environments were simulated: 1) a vapor environment consisting of the potential getter poisons in representative concentrations generated from the waste in a typical UST (McDuffie 1994), e.g., ammonia, nitrous oxide, and carbon monoxide, and 2) the waste environment, consisting of a simulated non-radioactive liquid waste, constructed from a hypothetical recipe representing a typical UST.

AS–KCD has already tested the effectiveness of DEB getter in a high radiation environment. Its performance begins to deteriorate noticeably when it is exposed to greater than 1000 Mrad of gamma radiation. Also, long term tritium (beta) radiation was evaluated prior to acceptance for the H1616 tritium shipping container (Gilliom et al. 1992). The radiation content in a transportation package will not exceed this value.

The synthetic waste used was a highly-saturated and alkaline aqueous solution with a 5-molar sodium ion concentration (Delegard 1994), the following table shows the constituents of the synthetic waste used to test the DEB getter, the quantities listed are for a one liter sample solution.

Table 1. Nominal Composition, Hanford Waste Solution Used as a Synthetic Waste for DEB Testing

Chemical	Concentration	Weight
$NaNO_2$	0.029 M	17.8 g
$NaNO_3$	2.44 M	207.1 g
$NaOH$	1.53 M	61.4 g
Na_2CO_3	0.06 M	6.5 g
$NaAl(OH)_4$	0.23 M	27.0 g
$Na_3PO_4*12H_2O$	0.13 M	49.4 g

Four evaluations on three getter configurations were performed to determine if certain gases generated by the radiolysis and thermolysis of liquid hazardous waste have a negative impact on DEB getter performance. Also, DEB getters were tested after being wetted by a simulated waste supernate.

The three getter configurations included: 1) a heat sealable polyolefin bag filled with five grams of granulated DEB getter, 2) five grams of 0.110 inch diameter by 0.120 inch tall right cylindrical pellets as produced for standard DOE production getter products, and 3) a silicone boot made from tough silicone rubber filled with one gram granulated DEB powder and capped with a thermoset plastic stopper. Five boots were used to keep the getter quantity constant at five grams per test.

The first two evaluations used standard AS-KCD getter production hydrogenation test equipment to establish a baseline for the three proposed getter configurations both wet and dry. This test equipment records the pressure change of a closed system that has a measured quantity of getter, a known volume and a specified initial pressure of 100% hydrogen gas. The system records the pressure change as the getter reacts and hydrogen is removed from the gas phase. The percent of reaction for a given getter sample is determined by pressure change and gas law calculations.

The last two evaluations used a special test set-up to evaluate getter performance when exposed to specific gas mixtures. The gases were selected based on underground storage tank measurements taken at the Hanford Site in Richland Washington. These gases were

evaluated individually with hydrogen and as a combined mixture to access any change in DEB getter performance. Also, several of the samples were subjected to the simulated waste to ascertain if the wetting of the DEB getter will substantially hinder the hydrogen-DEB reaction. The test atmosphere was measured for remaining hydrogen as percent by syringe extraction and analysis by gas chromatography.

Baseline testing in a 100% hydrogen atmosphere identified two items of interest. First, the silicone rubber in the boot is permeable to hydrogen but it does slow the hydrogen-DEB reaction down when the rate is compared to the granulated getter in a polyolefin bag or loose pellets in a sample tray. The slow down may be of no consequence when dealing with a gradual hydrogen production rate as opposed to the 100% hydrogen atmosphere used in this test. The second observation was that the getter does not readily wet when exposed to a simulated 5-molar sodium ion concentration of supernate synthetic waste (SW). The pellets float and the surface tension of the bag and boot prevents wetting by the solution.

The getter inside the bag will wet, however, when the liquid is forced inside the bag by vacuum. Vacuum is used at the beginning of all tests to remove oxygen prior to the addition of hydrogen. When tests were performed with the bag under a layer of SW after evacuation to 15-20 mm Hg, the rate of hydrogenation dropped considerably. However, when the same bag was re-tested wet only (not submerged) the rate doubled. Because the granules of getter were now wetted due to the previous applied vacuum the hydrogen was forced to diffuse through this liquid layer to reach the catalyst on the getter. Although the total uptake at 24 hours was only 20% of the value obtained by the dry bag, the rate of hydrogenation was steadily increasing over time. If the test had been continued for possibly 72 hours the getter would have reached the same total capacity as seen with the surface wetted part or dry part.

Testing with the gas mixtures expected to be generated during transportation of the liquid indicated that only carbon monoxide would be of concern for the getter. Carbon monoxide reduced the overall rate at which the getter would remove the available hydrogen but the CO did not stop the getter from reaching its hydrogen capacity. Typically with all the getter samples the hydrogen concentration would be reduced to levels below 0.1% within the first hour if CO was not part of the mixture. When CO (1% by volume) was part of the mixture, the time to achieve less than 0.1% remaining hydrogen would take from 2 to 10 times as long. The longer times were typically after the same getter had been exposed to CO twice before. Carbon monoxide does not appear to poison the catalyst. The reaction that occurs is more of a temporary blockage of the catalyst site by the CO as it is absorbed by the carbon portion of the catalyst mixture. It was also observed that the ammonia and nitrous oxide were absorbed by the carbon. However, no slowdown of the hydrogen-DEB reaction was identified when either or both of these gasses were present in quantities as high as 30% by volume.

When the gas inhibition tests were performed on SW wetted samples the same type of rate reduction as seen with the 100% hydrogenation tests were observed. The gettering rate was reduced but not stopped. The slowest rate occurred when the getter was tested when completely submerged. The same diffusion problem occurs where the hydrogen has to diffuse through the layer of liquid to get to the catalyst on the getter. When the excess fluid is shaken off or the part is allowed to dry the rate of reaction goes right back up to where less than 1% of the hydrogen remains after 1 hour exposure. When the boots are used the rate is further reduced because of the layer of silicone rubber. Repeated additions of CO slow the hydrogenation rate each time, but this type of test does not simulate the way the gasses would be generated from the actual hazardous waste liquid. Carbon monoxide would not be generated in large additions. The rate would be gradual and much less than the rate of hydrogen generation. The slowest tested rate in this study

is expected to be several time faster than the actual generation rate of both the hydrogen and the carbon monoxide.

The following chart represents the observed inhibition effects that CO has on DEB getter inside a polyolefin bag. The same observations were identified on the pellets and silicon boot parts. The pellets tracked at the same reaction rate, the silicone boot parts had an observed time lag of approximately 240 minutes to achieve the same level of percent hydrogen remaining. Note: When ammonia or nitrous oxide are part of the gas mixture the measured hydrogen values are higher because the overall volume of the mixture is reduced by approximately 5% due to the absorption of these gases onto the catalyst component of the DEB getter.

CHART 1.   Hydrogen Reaction (% Remaining)Vs Time with Different Gas Mixtures Using 5 Grams of DEB Inside a Dry Polyolefin Bag
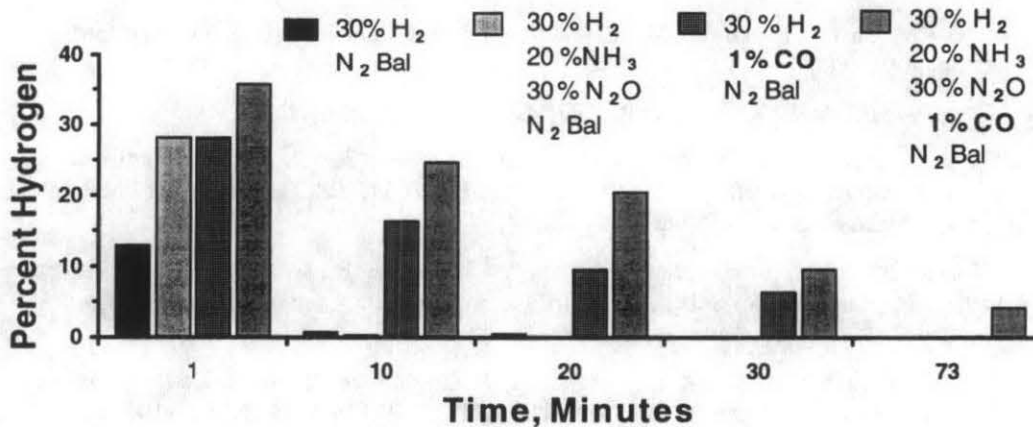
RECOMMENDATIONS

These studies assessed getter performance when the test atmosphere had been fully developed. Testing while the gasses are generated at the estimated evolution rate would provide the final evidence that the DEB getter will provide the required hydrogen mitigation. Also wet testing without vessel evacuation should be evaluated to ascertain if the hydrogenation rate changes observed would repeat if the parts had not been subjected to vacuum while in direct contact with the SW solution.

The recommended getter configuration for the transport of liquid waste would either be the polyolefin bag or the silicone boot. The pellets, although very reactive, would be an extra processing expense that appears unnecessary. The boot part kept the SW completely away from the getter, however the boot is an extra design feature that may also not be necessary. The boot configuration by design will have a slower hydrogenation rate due to the diffusion characteristics of the silicone rubber. The polyolefin bag, therefore, may well be the most cost effective and rate effective choice. The liquid waste did not soak through the material until vacuum was applied. Several layers of this material would keep the bag floating on the liquid or if desired the bag could be attached to both ends of the container. Possibly a long term test could be devised where several bags of DEB getter are placed in a simulated waste environment that would be agitated in a random fashion for a period of several months. The bags could then be evaluated for hydrogenation and integrity (radiation damage) at the conclusion of the cycle and compared to a control part.

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