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Proposal for Qualification of Gas-Generating Radioactive Payloads for Transportation within a Type B Package - The Recombiner/Getter Approach

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PROPOSAL FOR QUALIFICATION OF GAS-GENERATING RADIOACTIVE PAYLOADS FOR TRANSPORTATION WITHIN A TYPE B PACKAGE – THE RECOMBINER/GETTER APPROACH

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ABSTRACT

This paper proposes an alternative approach to qualifying gas generating radioactive payloads for shipment within Type B packaging through application of hydrogen recombiner/getter technology. This work compliments an earlier paper by the same author describing a direct measurement approach to achieving the same qualification goal. Specifically, this paper discusses another part of the success at the Savannah River Site (SRS) in authorizing onsite transfer of legacy Radioactive Materials (RAM) within the DDF-1 package. The current safety basis requires a measurement of storage can pressure and placement of a recombiner/getter product inside the package containment vessel to prevent significant hydrogen accumulation in the closed volume surrounding the storage can. These two actions are sufficient to ensure 1) that deflagration pressure of a potential flammable gas mixture is within Normal Conditions of Transport, and 2) the consequences of a detonation shock wave are within the Hypothetical Accident Conditions.

I INTRODUCTION

DOE-STD-3013-2000[1] describes the potential for high-pressure gas build-up in sealed containers of plutonium-bearing oxides. Clearly, pressure from radiolysis or chemical reactions with moisture and accumulation of flammable gas mixtures are issues that must be resolved as part of payload qualification for onsite transfer.

This paper is a companion to a previous work[2] and supplements the former development with an alternative approach that reduces the requirements for testing of the package content to solve the same problem. To limit repetition of program details, the reader is assumed familiar with the previous work. Briefly, missions within the Department of Energy (DOE) complex often require inter-site shipment of radioactive materials (RAM) over public highways. This paper describes an alternative means of qualifying RAM payloads of unknown moisture content for onsite transfer at the Savannah River Site (SRS) in the DDF-1 package and how the same process could be applied to offsite shipment. The core issue addressed by this paper is how to limit flammable gas concentrations and how to accommodate the corresponding consequences of combustion within a transportation package.

II ONSITE TRANSFER AT THE SRS – BACKGROUND

Ongoing as part of the Defense Nuclear Facilities Board (DNFSB) Recommendation 94-1, plutonium-bearing RAM in interim storage at the SRS is being consolidated and stabilized for long-term storage in accordance with DOE's 3013 standard. As cited previously,[2] the RAM in question has been in storage for an extended time period (often more than a decade), and the moisture content of these materials may exceed the criteria for *stabilized* materials in accordance with DOE-STD-3013-2000.[1] Therefore, the potential exists for generation of flammable gas mixtures within the storage cans by radiolysis of moisture to generate both hydrogen and oxygen gas. The storage cans, better known as convenience cans in RAM packaging vernacular, are not welded pressure vessels, consequently flammable gas produced by radiolysis or chemical reaction can leak into the containment vessel.

An important underlying requirement for onsite transfer of these materials at the SRS is the need to avoid re-canning the RAM. This requirement is driven in part by the site directive to maintain radworker dose as low as reasonably achievable (ALARA). Consequently, accumulation of generated gasses within a RAM storage can is anticipated, and the occurrence is detected using both radiography and the lid deflection technique[3] described previously.

[1] Currently only RAM compliant with DOE-STD-3013-2000 criteria is authorized for transport in the 9975 package. Testing conducted as part of establishing this standard demonstrated that properly stabilized residues that are packaged in an inert (helium) gas should not generate sufficient oxygen gas to support combustion of hydrogen in the 3013 vessel.

Two alternatives have been developed at the SRS for transportation of RAM without prior characterization of gas generation rate or gas composition.

One path discussed in a previous work uses a belljar for direct measurement of gas generation rates for the individual containers of RAM. Combined with an indirect measure of convenience can pressure (estimated by correlation of can lid deflection with pressure) the RAM contents can be shown to not exceed threshold values established for package safety.
A second and perhaps more shipper-friendly means of qualifying RAM for onsite transfer is the application of recombiner/getter technology described in this paper. The recombiner in this application is a precious metal catalyst that promotes the formation of water from hydrogen and oxygen gases in the local environment known as the containment vessel headspace. The water produced from recombination is adsorbed on a molecular sieve included within the recombiner/getter packet. The recombined water is held outside the convenience cans, away from the RAM and does not undergo further radiolysis. If oxygen is not present (or depleted greatly by recombination) within the containment vessel headspace, then the precious metal catalyst promotes the removal of hydrogen by irreversible hydrogenation of a butadiene polymer. This getter action removes hydrogen irreversibly from the headspace gases and is considered a defense in depth measure.

Application of the recombiner/getter product will prevent accumulation of flammable hydrogen and oxygen mixtures in the headspace of a containment vessel. However, flammable gas build-up within a convenience can must be acknowledged, and the consequences of combustion there must be shown not to compromise containment integrity. Specifically, the packaging containment vessels must be shown capable of sustaining the pressure pulse from deflagration within a convenience can and capable of sustaining the shock wave associated with a transition from deflagration-to-detonation.

III ONSITE TRANSFER AT THE SRS – ENABLING FEATURES

As described in a previous work,[2] the plutonium-bearing RAM stored at the SRS is housed in convenience cans described typically as a can/bag/can arrangement. In each configuration, the inner can, typically slip-lid style, is assumed to leak freely. The outer is a common food-pack style can closed by crimping the closure lid to the body of the can. The crimp seal retains radioactive solids satisfactorily, but may allow gases generated by radiolysis or other chemical reactions to vent at rates that vary with the internal pressure and the quality of the seal. The materials stored inside the cans are heads, tails, excess or residues from various nuclear material production campaigns or development programs around the DOE complex. Storage can pressures have been demonstrated to be at steady state by an SRS vault surveillance program that monitors can integrity on a periodic basis (including deflection of storage-can lids).

As cited in the previous work, a set of curves has been established relating measured changes in the curvature of the convenience can lid to internal pressure for the different styles of food-pack cans used at the SRS for material storage.[3] Internal pressure as low as three psig is discernable.

Belljar measurement and time-based limitation of gas accumulation within containment vessel headspace was discussed in the previous work. The time-consuming belljar measurement is unnecessary if flammable gas accumulation within the containment vessel is mitigated satisfactorily by the performance of included recombiner/getter materials. In this case, the pressure within a RAM storage can is the governing parameter in limiting the consequences of flammable gas combustion within a package.

Recombiner/getter qualification testing was carried out at the Savannah River Technology Center using an actual DDF-1 containment vessel and full-scale recombiner/getter product. This testing work investigated a range of behaviors deemed credible for the plutonium-bearing RAM payloads to be transferred onsite at the SRS (including the presence of potential poisons), and the results are documented in an extensive report on system performance.[4] The recombiner/getter product provides robust performance even under the bounding assumptions for gas generation from uncharacterized plutonium-bearing residues (unknown moisture content, rates or compositions of generated gasses).

Recombiner and getter performances are influenced by the rates of two chemical reactions promoted by the precious metal catalyst. The recombination reaction is somewhat sensitive to temperature variations and increases in rate with increasing temperature. The hydrogenation reaction is more temperature sensitive, and at sufficiently high temperature the polybutadiene polymer may begin crosslinking. Consequently, the thermal environment within the package may affect both hydrogenation rates and hydrogen capacities. The effects of temperature on getter performance have been studied in great detail and are presented in a recent report.[5] Hence, the thermal environment within the DDF-1 must be limited to ensure that the getter can function as an effective defense-in-depth safety system.

DOE Order 460.1A permits application of administrative controls in achieving equivalent safety for onsite transfers. For example at the SRS, package exposure to direct sunlight can be disallowed except briefly during placement within a conveyance that also shades the packages from insolation. Thereby any potential for unexpected, but packaging-induced[2] chemical reactions within the payload materials can be reduced or eliminated. Control of the local thermal environment is less critical for recombiner performance but may be significant in the performance of some hydrogen getters.

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2 The thermal environment within a package can be more severe than the thermal environment within a storage vault.

For the onsite transfer campaign discussed here, the absence of insolation helps ensure that the local thermal environment within the package will not trigger chemical reactions that could result in hydrogen generation faster than the recombiner/getter is sized to accommodate.

Conservative assumptions on the rate of hydrogen generation provide sufficient information to size a recombiner/getter product. The maximum period of time a primary containment vessel (PCV) may remain sealed for onsite transfer of its payload can be calculated based on the rate of hydrogen generation and the capacity of the getter. This application of recombiner/getter technology is part of the safety basis for onsite transfer of RAM-storage cans within the DDF-1 packaging.

IV DDF-1 PACKAGE

The DDF-1 is a prototype of the 9975 packaging, which is currently certified by the DOE for offsite shipment of up to 4.4 kg of plutonium metal or 5.0 kg of plutonium oxide. The DDF-1 name is an SRS nomenclature that represents a

Drum packaging with
Double containment vessels qualified for
Fissile payloads with nominal volume of
1 gallon.

A schematic representation of the DDF-1 is shown in Figure 1. The radioactive contents (plutonium metal or oxide) are housed typically within two nested metal cans as a handling convenience. A typical arrangement of payload cans and inside the PCV is shown in Figure 2 including typical placement of a recombiner/getter packet. The maximum allowable pressures within the PCV and SCV under regulatory Normal Condition of Transport (NCT) are unchanged from the 9975 package at 900 psig and 800 psig, respectively. Under Hypothetical Accident Conditions (HAC), the allowable static limit pressures remain 5500 psig and 5000 psig, respectively.[3]

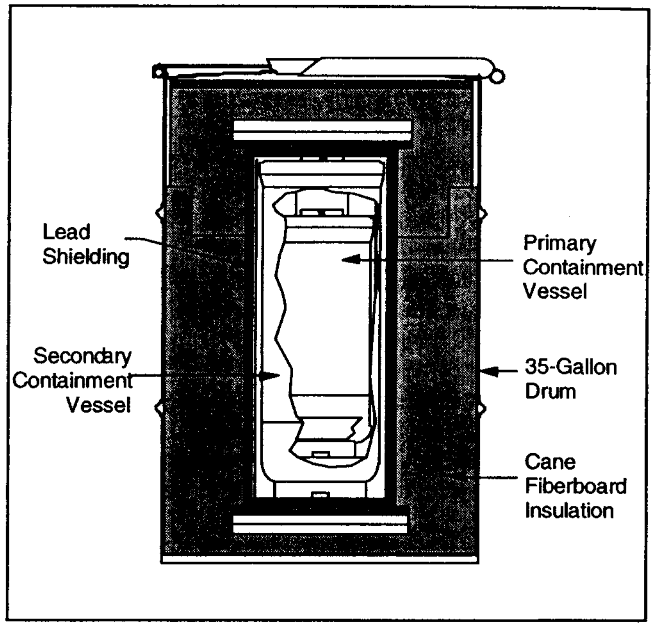

Figure 1 - Illustration of the DDF-1 Package

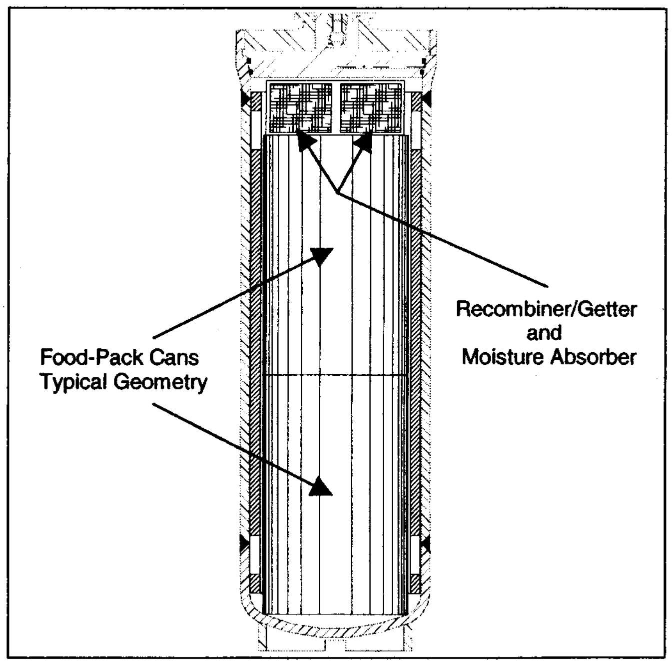

Figure 2 - Typical Arrangement of Payload Cans and Recombiner/Getter within the DDF-1 PCV

V ONSITE TRANSFER AT THE SRS – THE EVALUATION

In general, gasses generated by RAM in storage may accumulate within storage cans and/or escape to the surrounding environment. Because of this behavior, both the pressure and the composition of these gasses must be considered in evaluation of package safety. Specifically, accumulation of pressurized flammable gasses is possible

[3] The vessel closures are stronger than the vessels themselves.

within the storage cans and within package containment vessels, hence, both conditions are evaluated as part of the safety basis for onsite transfer of the RAM.

As cited in a previous work, the maximum pressure capacities of the DDF-1 containment vessels were established in accordance with Section III of the ASME Boiler and Pressure Vessel Code for NCT and Code Case 584 for HAC.[6] Based on the maximum allowable consequences of flammable gas combustion (deflagration and detonation), the maximum allowable initial conditions can be back calculated by assuming a worst-case gas composition.

As described in the previous work, the food-pack cans storing the RAM have done so for an extended period of time and pressures sustained by the cans are at steady state. The gas composition within the cans is assumed to be a stoichiometric mixture of hydrogen and oxygen. Calculation of the number of moles of gas in each can is based on the measured pressure and the assumption that solid content (i.e., plutonium-bearing materials, bags and slip lid cans displaces zero volume. Clearly, these are two very conservative assumptions.

The performance of the recombiner/getter easily accommodates normal leakage from food-pack cans into the PCV. The recombiner/getter materials have been qualified to remove hydrogen and oxygen from the local atmosphere and prevent the surrounding gas mixture from reaching the Lower Flammable Limit (LFL) of hydrogen in air. The performance of the recombiner/getter was demonstrated to provide satisfactory hydrogen removal for an encounter rate (composite leak rate from convenience cans) up to 14 STP cm^3 hr^{-1} over a period of 30 days. The getter alone is capable of removing more that 30 STP cm^3 hr^{-1} up to 90% of its rated capacity or a total of 15,120 STP cm^3 of gettered hydrogen. See the *Sizing the Recombiner/Getter and Moisture Absorber* section for additional details.

With the exception of a sudden rupture, the presence of recombiner/getter within the PCV renders the leak rate from a convenience can largely irrelevant. The assumption of an aqueous solution of the radionuclides, supports a bounding calculation of the hydrogen generation rate. For convenience cans at steady state pressure, the normal (isothermal) leak rates are equal to the combined gas generation rates for hydrogen, oxygen and other gases produced by radiolysis or chemical reactions. When hydrogen and oxygen are produced in stoichiometric proportions (H_2 + ½O_2), this mixture will recombine without consuming getter capacity. If only hydrogen is generated, then the oxygen content of air trapped in the PCV will be depleted by the recombination chemistry prior to consuming getter capacity.

<u>Normal Conditions of Transport</u>

Not surprisingly, the pressure pulse (a supersonic shock) resulting from a deflagration to detonation transition (DDT) has more severe consequences than the pressure generated by a simple deflagration. Hence, detonation of flammable gasses sets the maximum allowable initial conditions within a convenience can (stoichiometric mixture of hydrogen and oxygen with nitrogen absent). See the *Hypothetical Accident Conditions* section for discussion.

Maximum Normal Operating Pressure (MNOP) is evaluated as follows. Assume each of two sets of convenience cans is at thermal equilibrium inside the DDF-1 under non-solar NCT temperature and pressurized to the maximum permitted by the HAC (detonation) evaluation. Assume also that both sets of cans release their confined gasses suddenly (adiabatically) into the PCV. Assume the recombiner/getter continues to function but only at the rate prior to the sudden release. Assume all gasses mix completely. The resulting pressure (no combustion) is the MNOP at the average temperature within the PCV.

Worst case deflagration is evaluated as follows. Assume each of two sets of convenience cans is at thermal equilibrium inside the DDF-1 under non-solar NCT temperature and pressurized to the maximum permitted by the HAC (detonation) evaluation. Further assume the recombiner/getter has maintained the non-flammable character of the environment outside the cans (kept the hydrogen concentration below its LFL in air). Assume the gas mixtures within each of the cans are ignited simultaneously and burn to completion adiabatically within the cans. Assume the cans rupture only after maximum combustion pressure is achieved, then all gasses within the PCV mix completely. The resulting pressure at the average temperature within the PCV is the result of worst case of deflagration

The maximum deflagration pressure within a convenience can is calculated via the SRS proprietary KABOOM computer code. The code models the chemistry and thermodynamics of hydrogen-air combustion. The code calculates pressure peaks, but not pressure-time profiles, and accounts for: dissociation of water vapor into hydroxide, molecular hydrogen and molecular oxygen; dissociation of molecular hydrogen, molecular oxygen and molecular nitrogen; and the reaction that forms nitrous oxide.

As cited in a previous work, deflagration is a slow process relative to the natural frequencies of the DDF-1 containment vessels, and the pressure pulse will build too slowly to excite a dynamic resonance.[6] Therefore, no reduction in static pressure capacity is necessary to account for dynamic behavior of the vessels.

At the SRS for example, low-heat plutonium-bearing scrap materials (i.e., up to three watts) were qualified for onsite transfer in the DDF-1 package by a combination of lid-deflection measurement and accompaniment of a qualified recombiner/getter packet. As described above, maximum deflagration pressure results from complete combustion (without detonation) at the maximum allowable pre-detonation conditions. These conditions are simply the pressure and temperature of the stoichiometric hydrogen and oxygen inside a food-pack style convenience can. Outside of the cans ongoing recombination and gettering would mitigate the presence of these gasses, to the extent that combustion could not continue significantly beyond the volume of the can. MNOP and deflagration results within the PCV are given in Table 1. Also presented in the table are comparable results from the previous work[2] wherein flammable gas generation from the same package payload is measured directly and combustion consequences are controlled by time restrictions.

Compared to the allowable NCT pressure of 900 psig for the PCV, these deflagration events are sustainable under NCT and thereby do not compromise package safety. In addition, performance of the recombiner/getter is qualified[4] to remove hydrogen and/or oxygen gasses from the volume of the PCV to the extent that the remaining gasses are not flammable. Hence, discussions of flammable gasses leaking from the PCV into the SCV and the potential consequences thereof are unnecessary.

Table 1 - Maximum Non-Solar NCT Pressures

Condition	Recombiner/ Getter Approach PCV Pressure (psig)	Test Qualification Approach[2] PCV Pressure (psig)
Non-Solar MNOP [a]	9.7 (143°F) [b]	17.9 (122°F) [c]
Associated Peak Deflagration Pressure	134 [d]	252 [e]

[a] PCV static design pressure is 900 psig.

[b] Assumes two cans sustaining maximum DDT-based pressure release suddenly (adiabatically) into the PCV and complete adiabatic mixing of the gasses.

[c] Assumes two cans sustaining maximum DDT-based pressure leak slowly (isothermally) into the PCV and continue to generate H_2 and O_2, producing a pre- combustion pressure within the PCV that if detonated via DDT would generate the vessel limit pressure.

[d] Assumes complete combustion of stoichiometric H_2 and O_2 entirely within each of two cans sustaining the maximum DDT-based pressure, then mixing completely with PCV air surrounding the cans.

[e] Assumes complete combustion of generated H_2 and O_2 in PCV air (no DDT) at end-of-transfer MNOP.

Hypothetical Accident Conditions

Direct detonation of a pressurized, stoichiometric mixture of hydrogen and oxygen is not credible. However, the consequences of a shock wave resulting from DDT are evaluated, because preventative control of detonation cell size is not achievable within the convenience cans.

The maximum credible detonation pressure spike is developed independent of volume from the scenario wherein DDT occurs after 50 weight percent of the gasses has been consumed,[4] and the pressure is applied to portion of the vessel surface area.[7] The maximum allowable pressure from a DDT event is limited to the dynamic limit pressure of the PCV.

As described in the previous work,[2] dynamic limit pressures for the PCV and for the SCV are 3900 psig and 3550 psig, respectively.

The performance of the recombiner/getter is qualified[4] to remove hydrogen and/or oxygen gasses from the headspace of the PCV rapidly and to the extent that the remaining gasses are not flammable. Consequently the occurrence of a DDT event is limited to the moles of gas retained within the convenience can.

Consider a DDT event within a convenience can that is pressurized by an undiluted stoichiometric mixture of hydrogen and oxygen (i.e., nitrogen from air inside the can has been purged from the can by continuous production of gas over an extended period of time). The maximum allowable initial conditions within a convenience can are those that yield a detonation pressure spike equal to the PCV limit pressure.

For example, from the SRS low-heat plutonium-bearing scrap materials, the average gas temperature within a single maximum-heat can associated with non-solar NCT is 158°F.[5] The associated detonation spike can be calculated by the KABOOM computer code. Detonation of gasses at this temperature (via DDT) will yield the PCV's dynamic limit pressure if the can is initially at 15.3 psig. Hence, up to this pressure at 158°F, a detonation (via DDT) within a food-pack can will not compromise PCV containment performance.

Consider a DDT event within the PCV. A DDT event in the annular volume surrounding the cans could occur only if a can suddenly released its pressurized detonable mixture. A DDT event is then possible for a period of time before the transient performance of the recombiner/getter reduces the atmosphere within the PCV to a non-detonable condition (and later to a non-flammable condition). However, the reduced pressure and temperature of the detonable gas mixture (also diluted quickly by nitrogen from PCV air) means the pressure spike from a DDT event originating in this volume could not be more severe than that originating within a food-pack can before the sudden release. Hence, the effects of a detonation (via DDT) outside the convenience cans but within the PCV will not compromise PCV containment performance.

Consideration a DDT event within the SCV. If pressurized

[4] Delayed DDT increases the peak of the detonation pressure spike, because the reflected shock wave amplifies the pressure ahead of the flame front.

[5] Heat load for the DDF-1 thermal analysis includes both radioactive decay and recombiner/getter function at maximum reaction rate. The recombiner/getter heat generation is bounded by the recombination reaction followed by heat of adsorption for water on the molecular sieve.

detonable gasses accumulated within the PCV and were released into the SCV before combustion,[6] the mixture would be reduced in both temperature and pressure and diluted further with nitrogen from air contained within the SCV. However, evaluation of this behavior is unnecessary, because the performance of the recombiner/getter is qualified[3] to remove hydrogen and/or oxygen gasses from the PCV to the extent that the remaining gasses are not flammable. Non-flammable gasses leaking from the PCV into the SCV are not a combustion hazard and no additional discussion is necessary.

Note that the convenience cans house the sources of the gas generation and primary sources of heat (recombiner/getter heating occurs outside the cans). Hence, while packaged inside the DDF-1, can pressures will remain greater than or equal to the pressure within the PCV volume surrounding the cans. This means that for the pre-combustion pressure within the PCV to exceed the 9.7-psig value given in Table 2, the pressure within the convenience cans would have to exceed its maximum allowable value. Therefore, only those conditions within the food-pack cans are relevant to the maximum allowable detonation pressure (from a DDT event) within the PCV.

Table 2 - Maximum HAC Pressures

Condition		PCV Pressure (psig)
Static Limit Pressure [a]		5500
Dynamic Limit Pressure [b]		3900
DDT Location	Maximum Initial Pressure (psig)	Peak Detonation Spike [c]
Inside Food-Pack Can at 158°F N_2 absent, + Stoich. H_2 & O_2	15.3	3900
Inside PCV at 143°F [d] (Sudden Release from Food-Pack Cans): N_2 & O_2 normal vessel air, + Stoich. H_2 & O_2	9.7	< 3900

[a] Based on minimum vessel wall dimensions and 5% hoop strain.
[b] Based on application of Dynamic Amplification Factor of 1.41.
[c] DDT after 50 weight % of the combustible gas mixture has been burned by deflagration.
[d] Assumes two cans sustaining maximum DDT-based pressure (H_2 and O_2) release suddenly (adiabatically) into the PCV air, suddenly mix completely, ignite, burn and detonate.

For example, a large number of the SRS low-heat plutonium-bearing scrap materials are at steady state pressure within the storage cans following extended storage. Food-pack cans showing less than 15.3 psig at 158°F (12.5 psig at 100°F) are acceptable for packaging and onsite transfer without further testing as long as a properly sized recombiner/getter packet accompanies the cans as part of the package payload.

<u>Sizing the Recombiner/Getter and Moisture Absorber</u>

The physical dimensions of the recombiner/getter packet used in the DDF-1 package were limited to those that leave sufficient volume within the PCV to receive two typical food-pack cans of RAM. This arrangement supports onsite transfer of roughly one kilogram of weapons grade plutonium-bearing scrap. If the payload is limited to a single convenience can, the size of the recombiner/getter packet can be enlarged or additional packets added to provide higher hydrogen removal rates and higher hydrogen capacity. At present, the recombiner/getter product qualified for service in the DDF-1 is based on a commercial product developed and produced for use in vacuum insulation panels.[7] Continued development incorporating improved formulations of the polymer-based getter has improved getter performance significantly. These improvements may be applicable to future needs for onsite transfer of RAM at the SRS. In addition to 140 grams of the polymer-based hydrogen getter, the recombiner/getter packet includes 100 grams of 4Å molecular sieve to adsorb water resulting from recombination of hydrogen and oxygen. The molecular sieve will hold in excess of 15 grams of water and maintain the water vapor content within the PCV below one percent relative humidity (at 77°F). The current recombiner/getter packet is approximately four inches wide, six inches tall and 1½ inches thick and resembles a large tea bag. Note that these dimensions were demonstrated to not be critical to recombiner/getter performance.

The total hydrogen generation rate of the payload determines the recombiner characteristics necessary to prevent accumulation of flammable gasses within the PCV. The hydrogen capacity of the getter is a defense-in-depth measure to prevent hydrogen accumulation within the PCV after the recombiner has consumed the oxygen from the headspace. Taking no credit for the recombination reaction, the time span the DDF-1 containment vessels may remain sealed for onsite transfer is determined conservatively by the hydrogen capacity of the getter. If the hydrogen generation rate per watt of payload materials is not known, the value associated with aqueous solutions of the radionuclides will ensure conservatism.

For example, alpha radiolysis of water produces hydrogen gas with a maximum g-value of 1.6 molecules per 100 electron volts of absorbed dose. Calculation of gas generation rates assumes the water absorbs 100 percent of the alpha dose. The assumption of 100 percent absorbed dose is very conservative and combined with the maximum g-value of 1.6 may yield gas generation rates two or three orders of magnitude greater than actually observed under laboratory test conditions.

[6] Detonable gasses could not reach the SCV without simultaneous catastrophic failures of a pressurized food-pack can and the PCV.

[7] Polymer-based hydrogen getters were developed and patented by Dr. Tim Shepodd at Sandia National Laboratory and produced under license by Vacuum Energy, Inc. of Cleveland, OH.

Implementation Example

Figure 3 illustrates the relationship between the total heat per package payload (normally two sets of convenience cans plus a recombiner/getter packet) and the maximum allowable time the containment vessels may remain sealed for onsite transfer. Each curve in the figure represents a hydrogen generation rate expressed as a function of payload wattage to simplify determination of onsite transfer window. Given convenience cans at acceptable pressures, the curves are defined by the capacity of the getter and the hydrogen generation rates for the two material types.

The calculated maximum hydrogen generation rate for an aqueous solution of plutonium radionuclides is 14 STP cm^3 hr^{-1} $watt^{-1}$. The other gas generation rate cited in the figure is 5.6 STP cm^3 hr^{-1} $watt^{-1}$ or four times greater than the highest hydrogen generation rate observed from a solid mixture of plutonium oxide-bearing residues in laboratory tests.

The lower curve bounds the behavior of RAM with "unlimited" moisture content. The horizontal portion of the lower curve represents the maximum steady state hydrogen generation rate (30 STP cm^3 hr^{-1}) for which the recombiner/getter was qualification tested. Hence, to prevent exceeding this limit, the aqueous solution curve (14 STP cm^3 hr^{-1} W^{-1}) limits heat load to 2.2 watts. The upper curve is based on experimental observations and is a conservative estimate for the behavior of low-fired mixed plutonium-uranium oxide scrap. The horizontal portion of the upper curve represents the maximum package heat load for which the recombiner/getter was tested.

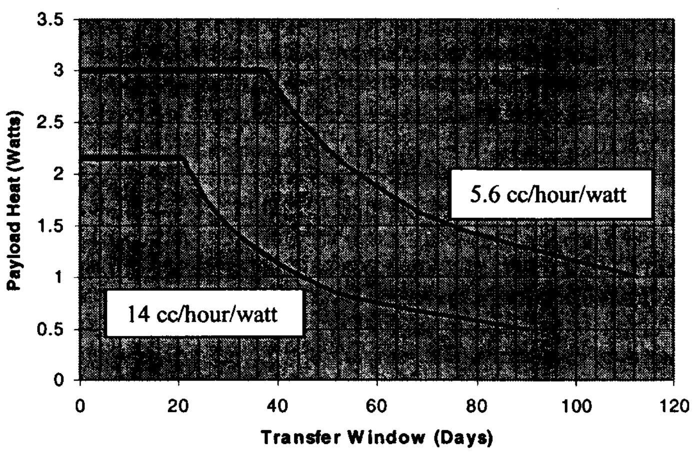

Figure 3 – Onsite Transfer Window for Payload Hydrogen Generation Rates

Consider a payload of food-pack style convenience cans housing SRS low-heat plutonium-bearing scrap materials. Assume the pressure within the cans is below the maximum allowed from Table 2. An onsite transfer window of 30 days is permitted if the total heat from a payload of unknown moisture content (lower curve given in Figure 3) is less than 1.5 watts. Viewed another way, the recombiner/getter was sized to permit packaging 2.2 watts of SRS plutonium-bearing scrap materials with unlimited moisture content and support a transfer window of 20 days.

Further, if the hydrogen generation rate of a payload can be bounded defensibly as suggested by the upper curve in Figure 3, then both payload heat and/or transportation window may be increased accordingly.

VI ONSITE TRANSFER AT THE SRS – CONCLUSIONS

In previous work,[2] RAM of unknown moisture content was qualified for onsite transfer at the SRS by measurement of pressures within storage cans (lid deflection) and measurement of leak rates from storage cans (belljar). This paper presented an alternative approach to solving the same problem. In place of time consuming belljar measurements, recombiner/getter technology was applied as follows.

RAM residing in food-pack style convenience cans has been in storage at the SRS for over a decade and shown by surveillance to be at steady state pressure. Gasses generated by radiolysis of unquantified moisture within convenience cans were assumed conservatively to be stoichiometric mixtures of hydrogen and oxygen. As in the previous work, pressures within food-pack style storage cans are determined by lid deflection measurements.[3] Cans showing less than the maximum allowable pressure are candidates for onsite transfer in the DDF-1 package. In practice, however, storage facility limits on convenience can pressure may be more restrictive than those of the DDF-1 package.

Assuming flammable gas generation within the package payload, both deflagration and detonation (via DDT) of flammable gas mixtures were considered and the pressures resulting from these events were evaluated. The structural and containment capacities of the DDF-1 containment vessels limit the maximum allowable pressure associated with a DDT event within the package as a credible accident condition. Assuming complete combustion (without DDT), the maximum deflagration pressure within the package was evaluated as an off-normal event but within the non-solar NCT performance capability of the DDF-1 package.

Supporting the structural calculations, a qualified recombiner/getter packet must be included in the PCV with the convenience cans as part of the payload. The recombiner/getter consumes hydrogen and oxygen gasses that leak from the cans and maintains the hydrogen concentration in the volume surrounding the cans below the LFL. Hence, the worst-case combustion events occur inside a convenience can containing a stoichiometric mixture of hydrogen and oxygen gas void of nitrogen or other diluent gas.

The length of time a payload may remain packaged for onsite transfer is determined by the maximum credible rate of hydrogen generation and the capacity of the getter without credit for recombination using the oxygen from air trapped in the PCV. Highly conservative estimates of hydrogen generation rates were provided graphically to facilitate development of transfer windows and to ensure that the atmosphere within the containment is not flammable when opened.

In summary, maximum normal operating pressure (MNOP), worst case deflagration pressure and worst case shock wave from transition from deflagration to detonation were calculated conservatively, compared to allowable values and shown to be acceptable for onsite transfer at the SRS. Inclusion of a qualified recombiner/getter packet as part of the package payload eliminated the need to know the gas leakage rates from candidate convenience cans. Hence, time consuming belljar measurements of gas leakage from cans are unnecessary. However, measurement of can-lid deflections remains necessary to enforce the maximum allowable pressure within convenience cans. Finally, avoidance of hands-on work to characterize and possibly repackage the RAM supports the DOE program to keep radworker dose as low as reasonably achievable (ALARA) while helping the SRS operating divisions to meet DNFSB 94-1 objectives.

VII RECOMMENDATIONS FOR APPLICATION TO SHIPMENTS IN COMMERCE

The following discussion identifies by section title the major differences between onsite transfer at the SRS and shipment in commerce over public highways. Specifically addressed are those package performance features or payload behaviors that did not need evaluation for the SRS example.

Influence of Regulatory Thermal NCT

As cited in the previous work, offsite shipments do not qualify for the privilege of equivalent-safety permitted by DOE Order 460.1A and must comply with the HMR explicitly. Hence, regulatory NCT must be used to determine the local thermal environments within a loaded package. Qualification testing of recombiner/getter performance would have to be carried out within a thermal environment representative of the PCV under regulatory NCT. If lacking characterization data, the RAM itself may need to be tested similarly to ensure that chemical reactions unknown in the thermal environment of a storage vault are not stimulated in the higher temperatures associated with regulatory NCT.

The maximum average gas temperature currently recommended for satisfactory functioning of the polymer getter is 158°F. Utilizing the recombiner/getter packet as described in this paper, the maximum allowable heat-load for a DDF-1 payload is estimated roughly to be six watts.

Consideration of higher temperatures requires a different recombiner formulation that would use an inorganic support precious metal catalyst(s). For example, platinum on alumina can recombine hydrogen and oxygen gasses at elevated temperatures. However, this formulation does not incorporate a getter for hydrogen removal when oxygen is not present. Other commercial catalysts can remove hydrogen from headspace gas using either oxygen from the headspace or oxygen from the molecular structure of the catalyst. These catalysts can provide hydrogen removal rates at higher operating temperatures equivalent to the recombiner used in the DDF-1.

RAM Cans Not at Steady State

In the event that steady state conditions are not defensible for the RAM stored within food-pack cans, at least two measurements of lid deflection will be necessary to establish a rate of pressure increase. The time between lid deflection measurements may need to be longer than the duration of the planned shipment window to demonstrate that pressures within the cans upon arrival at the destination will remain within acceptable limits for flammable gas combustion.

As an alternative, RAM may be re-canned with appropriately sized filter-vents in both the outer can and inner contamination-control bag – similar to materials developed for holding TRU wastes in the TRUPACT-II. Vented cans will release hydrogen as produced and prevent accumulation of a flammable gas mixture in the convenience can. Implementation of this consideration would eliminate the need for evaluation of DDT within convenience cans and provide a packaging configuration that is based on currently accepted storage practice.

NCT Vibration

As cited previously, empirical data from SRS surveillance of plutonium-bearing RAM in storage has shown that storage-can lid deflection (bulge or dish) may change from one stable value to another.[3] Regardless of the cause of this behavior, a recombiner/getter sized to accommodate gas generation from an aqueous solution of radionuclides will also accommodate gas generation from solids regardless of amount of over-the-road vibration.

SST Loss of Cooling Accident (LOCA)

As cited in the previous work, a simple and conservative method of analysis evaluated the 9975 package under a loss of cooling event within an SST.[8] The response of the 9975 package demonstrated a temperature increase of roughly 1¼ °F $hour^{-1}$ for the maximum heat load of 19 watts. Package payloads incorporating polymer getter materials (recombiner function does not depend on a polymer) must be temperature-limited to prevent compromising the function of the getter. In addition, under elevated temperature conditions, hydrogen generation from chemical reactions not observed under storage conditions may generate hydrogen much more rapidly than expected from radiolysis of water. Consequently, loss of cargo cooling within an SST may need consideration, and special preventative or mitigative measures may be necessary to avoid potentially unacceptable consequences.

Regulatory acceptance

The evaluations of gas generation presented in the previous work[2] and in this paper are very conservative in that the payload solids were assumed to displace zero volume. Additional conservatism is present in the assumption that generated gasses are hydrogen and oxygen in stoichiometric proportions. Oxygen gas is not a direct product of radiolysis of water and is typically only observed when plutonium-bearing oxides are not adequately calcined or have very high moisture contents following an aqueous process.

As cited in the previous work, dynamic capacities of the 9975 containment vessels have been demonstrated analytically but not by testing. An actual detonation test may be necessary to satisfy regulatory packaging authorities.

Assuming the requirement for double containment of dispersible solid plutonium. is removed[9] from the HMR, a new role for double containment could be offered. The SCV could be credited for regulatory containment of the payload, while the PCV could be credited for containment and attenuation of a detonation pressure spike. This notion could provide a substantial measure of defense-in-depth against the consequences of a detonation within a package and support the DOE program of maintaining dose to radworkers ALARA by minimizing the hands-on work needed to characterize and possibly re-can the RAM.

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