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Use of Hydrogen Getters for Ensuring Safe Storage of Plutonium-Bearing Materials at the Savannah River Site

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Abstract

Plutonium oxide left over from the 3013 destructive surveillance process is ultimately disposed of as waste. Therefore, this material is not re-stabilized and packaged to meet the requirements of DOE-STD-3013. Instead, it is stored on an interim basis in compliance with the interim safe storage criteria issued by DOE in January 1996. One of the safe storage criteria requires actions to be taken to minimize the formation or accumulation of flammable gases inside the storage container. Personnel responsible for the safe storage of the material have chosen to use a polymer-based, ambient air compatible hydrogen "getter" to prevent the formation of hydrogen gas inside the storage container and thus prevent the formation of a flammable gas mixture. This paper briefly describes the method in which the getter performs its functions. More importantly, this paper presents the results of the testing that has been performed to characterize the bounding effects of aging and demonstrate the use of the getter for long-term storage. In addition, the favorable results of a post-storage analysis of actual getter material are presented and compared with bounding predictions. To date, bounding test results have shown that after 18 months of continuous storage and 39 months of total storage at 70°C, the getter is able to both recombine gaseous hydrogen and oxygen into water when oxygen is available, and irreversibly getter (i.e., scavenge) hydrogen from the vapor space when oxygen is not available, both under a CO_2 environment. Further bounding testing has been deemed unnecessary, and continued post-storage testing will be conducted on a periodic basis. The first post-storage testing of deployed getter material after two years of service revealed that it still performed like new material.

Introduction

The United States Department of Energy (DOE) has promulgated requirements for the safe and long-term storage of plutonium (Pu) in various DOE nuclear facilities. These requirements are provided as DOE-STD-3013 (hereafter noted as 3013). Material preparation and packaging are two key aspects of the 3013 Program to ensure that hazards associated with the storage of Pu oxides are minimized. Another aspect is the requirement to perform periodic surveillance on representative items in storage to determine if any degradation mechanisms are at work that could jeopardize the remaining stored quantity. Results from the DOE Complex-wide 3013 Program have been documented in the two most recent publications of *Journal of Nuclear Materials Management* (JNMM). These publications have been focused almost exclusively on a variety of technical aspects of the 3013 Program across the DOE Complex. Therefore, only brief descriptions of the 3013 Standard and related packaging and surveillance activities will be provided in this paper. Given that the 3013 Standard covers long-term storage and surveillance of both solid metallic and oxidized Pu-bearing materials, and that both activities are primarily taking place at the Savannah River Site (SRS), the focus of this paper is an often overlooked aspect of the overall 3013 mission: post-surveillance storage of Pu-bearing oxide remaining from the destructive examination process. Specifically, a unique application of hydrogen getter technology has been employed to prevent the formation of hazardous and flammable atmospheres inside interim storage containers.

Surveillance and Packaging Details

An effort was initiated several years ago to consolidate surplus Pu-bearing materials at the Savannah River Site (SRS) at the K Area Complex (KAC) facility, formerly an operating reactor facility and currently a nuclear materials storage facility operated by Savannah River Nuclear Solutions (SRNS).

Figure 1: The K Area Complex (KAC) at the Savannah River Site (SRS)

Pu-bearing materials stabilized and packaged in compliance with the 3013 standard from both the SRS production facilities and other DOE Complex Sites (e.g. Hanford, Rocky Flats, and Lawrence Livermore National Laboratory) have been received at and stored in KAC. As a result of the surveillance activities performed at KAC and sample analyses at the Savannah River National Laboratory (SRNL), the DOE Complex is gaining a wealth of knowledge about how 3013-compliant materials behave while in long term storage. The surveillance activities include taking head gas samples, Pu oxide samples, and dissected pieces of the 3013 storage containers for analysis at SRNL. After the oxide samples are sent for analysis, significant quantities of oxide remain and must be safely stored until disposition in the HB-Line facility of SRS. For this interim situation, DOE has provided requirements for storage of Pu-bearing materials known as the Interim Safe Storage Criteria (ISSC). Where the 3013 standard requirements are intended to provide for material storage of 50 years, the ISSC were only intended for up to 20 years. KAC

has developed a program to ensure that all ISSC requirements are met during post-DE storage of Pu oxide. The storage container utilized in KAC is the 9975 shipping package, which is a double-containment stainless steel (SS) Type B package utilized by the DOE Complex partners for shipping fissile materials. Inside the primary containment vessel (PCV), Pu oxide is packaged into a three-layer arrangement consisting of a HEPA-filtered stainless steel inner can, a HEPA-filtered polyethylene bag, and a vented/filtered stainless steel outer can. This configuration allows the multiple gas spaces to interact and quickly become well mixed.

Hydrogen Hazards

One of the most significant hazards of storing Pu oxide is the generation of hydrogen as a result of radiolysis of moisture adsorbed on the oxide. When the radiolytic decomposition of water occurs, potentially flammable concentrations of hydrogen and oxygen may be reached if no venting capability exists. To minimize this concern, the 3013 standard places a limit on the amount of moisture as a function of the overall oxide mass (0.5 weight % moisture), and the storage cans are typically inerted for welding and transportation in a 9975. However, when the 3013 containers are opened in the glovebox environment in KAC, the oxide is exposed to relatively humid air and will have the opportunity to adsorb additional moisture. Since the facility does not have a furnace for restoring 3013 compliance, the potential for hydrogen generation must be controlled to maintain safe storage and meet the ISSC program requirements of preventing flammable gas concentrations. Calculations have been performed to address the gas generation rates with respect to reaching the lower flammability level (LFL) of hydrogen, assuming that enough oxygen is present in the storage containers to sustain combustion. The results of these calculations show that in order to maintain each storage container below the LFL, KAC personnel would need to open the containers for venting at highly impractical frequencies. Since the same personnel and facility location are utilized for the initial packaging and venting/repackaging, parallel surveillance and frequent venting activities simply cannot be sustained.

Hydrogen Hazard Mitigation

In an effort to seek alternative mitigation strategies, KAC personnel investigated a number of options. The option ultimately chosen was to utilize a commercially available polymer-based hydrogen getter material designed by Sandia National Laboratory[1], used in conjunction with a molecular sieve (zeolite) material. This particular material works in two ways depending on the environment. In the presence of both hydrogen and oxygen, its precious metal catalyst recombines the elements into water at a nearly instantaneous rate, with the formed water being subsequently adsorbed onto the molecular sieve. This is accomplished without any reduction in the material's "gettering" rate, which is the rate at which hydrogen is removed from the environment in the absence of oxygen via an irreversible, organic saturation reaction (see Figure 2). Each of these reactions is accomplished in atmospheric conditions at a wide range of temperatures with few known hindrances.

[1] Sandia's getters are commercially available from Vacuum Energy, Inc. (www.h2getters.com).

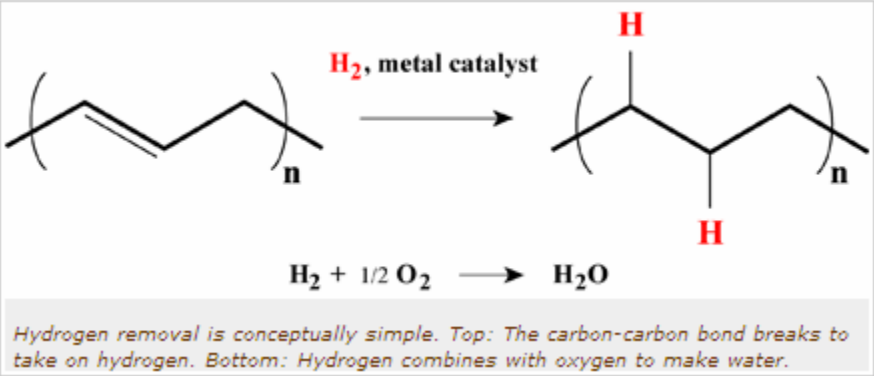

Figure 2: Two hydrogen removal mechanisms provided by Sandia's hydrogen getter

Although getter technology is not new, the use of getters for the storage of Pu oxide is believed to be a unique endeavor. Generally, polymers are strictly limited inside Pu-bearing material storage containers due to potential radiolytic degradation leading to hydrogen generation, and also due to concerns with neutron moderation enhancing the potential for criticality. In order to mitigate a conservative quantity of moisture, the design quantity of getter needed to be analyzed for these concerns. Polymer degradation from alpha radiation was not an issue since the Pu oxide is packaged in isolation from the getter by means of the vented and filtered cans and bags already described (see Figure 3). A perforated stainless steel can holds the getter and molecular sieve materials and sits on top of the outer can, directly above the outermost filter, and fills the majority of remaining space inside the PCV. A criticality analysis demonstrated that criticality is impossible even in the event of an unlikely getter/Pu oxide interaction. Still, questions remained and needed to be addressed about the viability of this option.

Figure 3: Filtered product can, bagout bag, outer can, and getter assembly (L-R)

First, both the 9975 safety documentation and ISSC program require that the storage containers be inerted to reduce the likelihood of flammable conditions. For 9975 packages, carbon dioxide is often used as the inerting agent and was required for this storage application. The inerting procedures utilized in KAC cannot guarantee 100% inerting, and therefore abundant oxygen for flammability must be assumed. This is mainly because a pressurized fill-and-evacuate technique is not available, and a simple gravity fill of an open vessel is used as the inerting process. This process will leave air inside the inner containers instead of fully completing a gas exchange, but a calculation has demonstrated that the entire PCV can be considered well mixed in less than 24 hours regardless of actual gaseous constituents. Sandia had never tested the performance of the getter in the presence of an abundance of both oxygen and carbon dioxide, and therefore could not guarantee adequate hydrogen removal. Second, although the getter is used by various industries at high temperatures, performance had never been quantified after continuous exposure to the temperature that is assumed to be an upper bound for storage. Third, the getter had to remove hydrogen at a rate that would maintain the hydrogen and oxygen concentrations below the LFL at any given time. Finally, the getter must provide a long period of time before the facility would need to vent the storage containers.

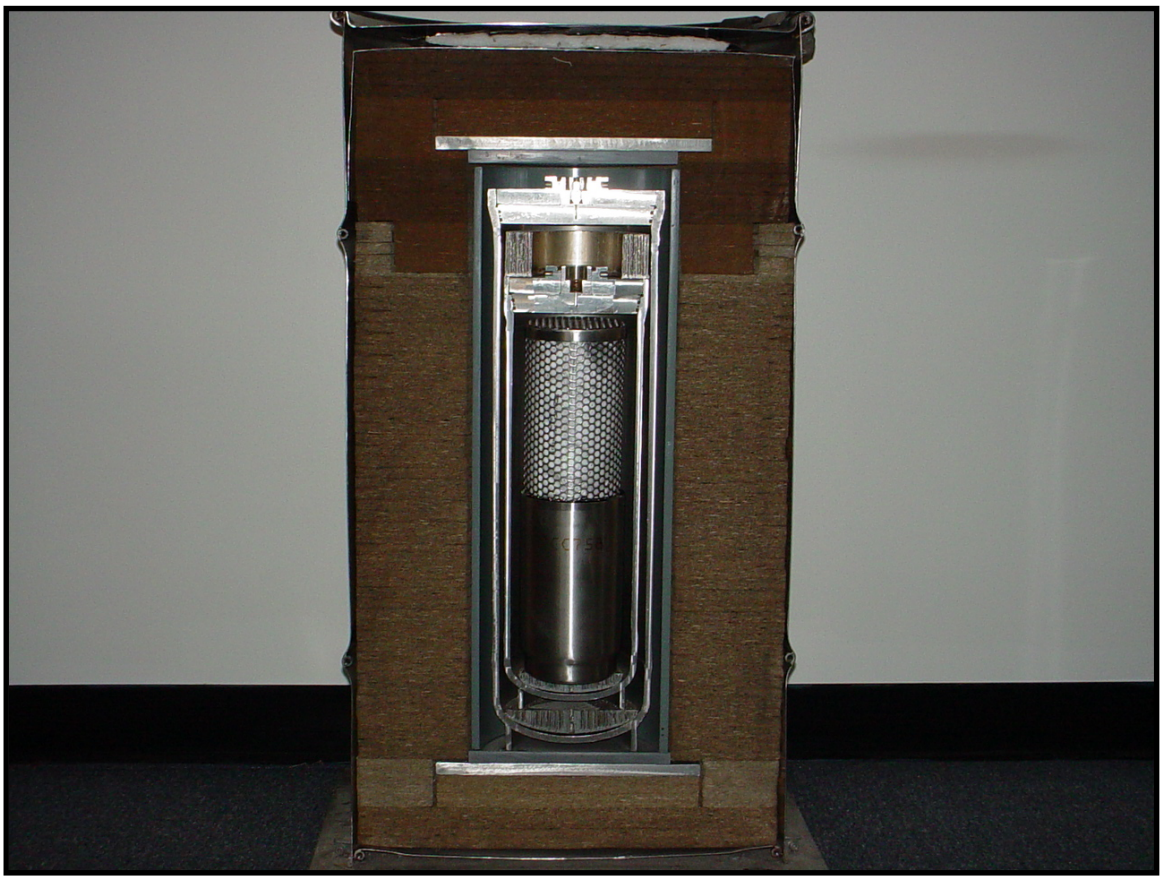

Figure 4: Cutaway view of the product can and getter assembly deployment

Hydrogen Getter Testing

SRNS commissioned Sandia to test each of these parameters in addition to providing technical expertise. An initial series of tests[2] was conducted in late 2006 on getter that had been aged for three months in an oven at 70°C. This is a standard temperature that Sandia uses to evaluate getter performance. As an implementation action, KAC personnel performed a thermal analysis of the storage vault and determined the maximum Pu oxide heat load per container that would keep the getter temperature below 70°C given conservative environmental conditions and limited ventilation controls. The test apparatus and conditions used by Sandia are conservative with respect to the packaging configuration and actual facility conditions. This is mainly due to hydraulic restrictions in the test apparatus that do not exist in the 9975 storage container. For example, in the test apparatus a small amount of getter was instantly exposed to hydrogen in excess of the LFL concentration, but the rate of removal was impeded by the somewhat tortuous access provided. In the storage facility, the initial concentration of hydrogen is negligible. As it is produced, hydrogen escapes the inner containers via the filters prior to reaching the LFL and interacts with the getter in a very short amount of time. It is also able to interact with a large surface area of getter. As previously mentioned, the primary KAC requirement was to prevent the formation of a flammable gas concentration inside a 9975. For this reason, and because of an initial quantity of oxygen present, the tests focused on the recombination function of the getter. This function removes hydrogen from the gas space as it is produced, but also reduces overall pressure as it recombines hydrogen and oxygen. Upon oxygen depletion from the gas space, any hydrogen accumulation that is not gettered would not lead to a flammable mixture since oxygen must be present to support combustion. If more hydrogen was produced than the getter could remove via gettering, or if the getter's hydrogen removal rate was slower than the generation rate, the resultant gas mixture during and after total radiolysis would still be non-flammable in storage. Facility procedures exist for safely venting them in this state. KAC personnel specified a quantity of getter with a sufficient removal rate to avoid this condition, but the justification exists for continued safe storage in case it occurs.

The initial tests were conducted to ensure that the getter would remove hydrogen in the presence of carbon dioxide after three months of aging at 70°C. Multiple runs with subsequent data analysis revealed that the getter recombined at an extremely fast rate (orders of magnitude faster than the assumed bounding generation rate), and gettered at a rate slightly slower than the bounding generation rate. KAC personnel also commissioned SRNL to irradiate a sample of getter to further simulate storage conditions. The cumulative gamma dose the getter sample received was far in excess of the expected dose when deployed. The irradiated samples were then tested by Sandia. The results of these tests were also favorable, and the getter was shown through nuclear magnetic resonance (NMR) to be structurally and functionally undamaged. Both Sandia and KAC personnel concluded that the getter would have no difficulty keeping the PCV gas space below the LFL in all cases, and in all but bounding conditions would remove all postulated quantities of hydrogen that could be generated at the rates it could be generated. After the initial series of tests, Sandia placed the remaining samples back into the oven at 70°C, but also placed a sample in a separate oven at 150°C to investigate later the effects of a postulated higher storage temperature.

[2] SAND2007-0095

In early 2007, Sandia conducted additional tests[3] on the getter aged at 70°C after it had been at temperature for six months. Shortly thereafter, samples were obtained and tested[4] from the getter aged for three months at 150°C (a far worse than expected temperature). In both cases, the additional time and temperature revealed that the getter continues to remove hydrogen both via recombination and gettering. Sandia continued a periodic testing program and the most significant result of these tests is shown below in Figure 5. The immediate pressure drop (from about 765 to 600 torr) is an artifact of the apparatus, but the evidence of hydrogen and oxygen removal is the pressure drop from about 600 to 565 torr in the first 1500 minutes. This particular group of tests was performed at an apparatus temperature of only 20°C to be conservative, since the rate is faster at higher temperatures. The legend of the graph indicates the aging conditions. Over three years of aging at bounding temperatures produced negligible degradation in hydrogen removal capability.

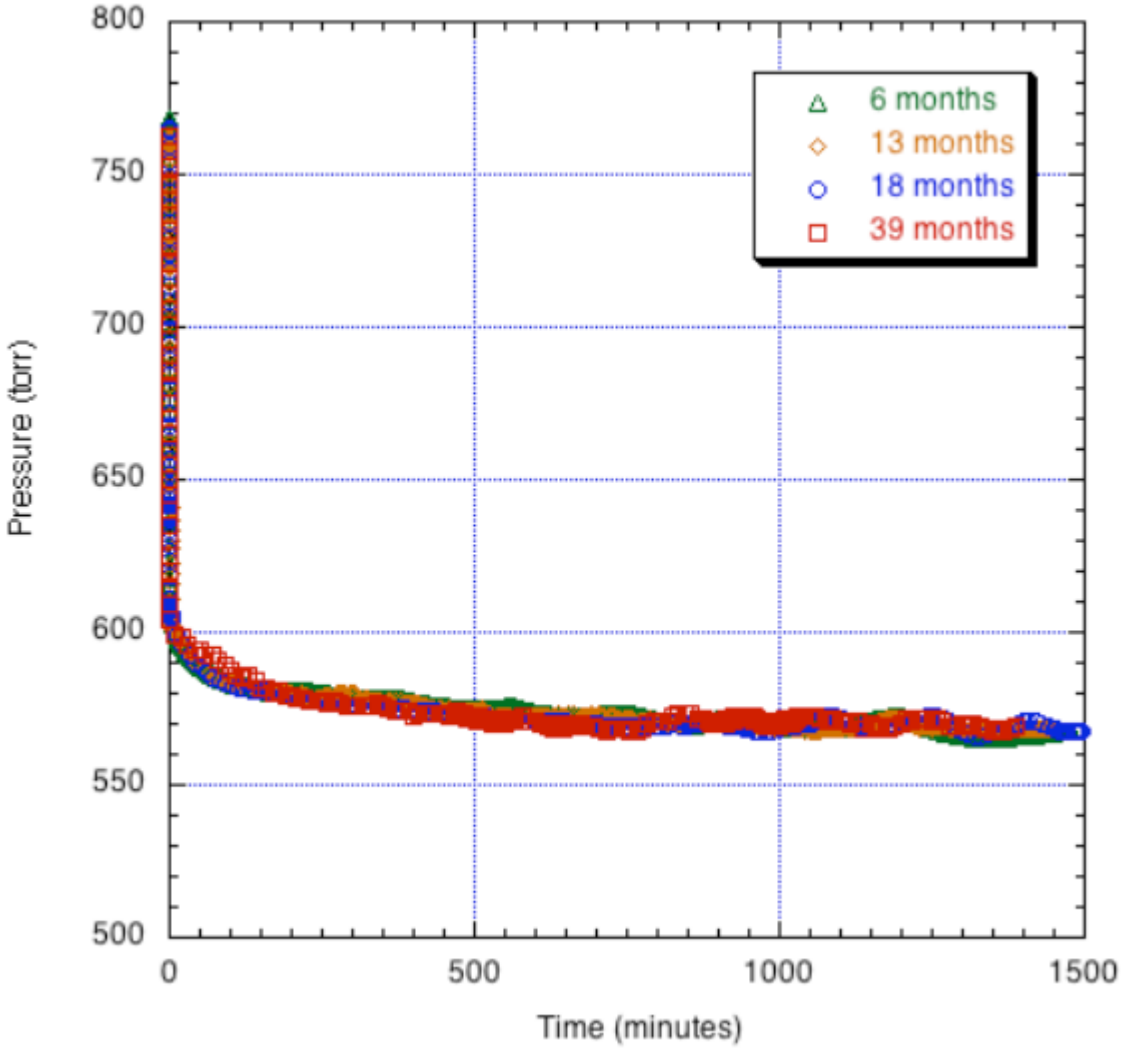

Figure 5: Summary of testing with getter aged at 70° C

[3] SAND2007-1789P
[4] SAND2007-3226P

In August 2008, Sandia researchers issued a report on the testing program for laboratory aged material[5]. All testing confirmed that periodic testing was no longer needed due to the observation of no significant degradation. The report concluded that "…biannual testing is no longer necessary due to the robust performance of the getter material, the very unlikely potential that the recombination reaction will fail during storage conditions in KAC, and the insignificant aging effects that have been seen in the testing to date." This was the desired conclusion from the testing endeavor. However, while this positive result was utilized, KAC desired to have confirmation that actual deployed material was tested to ensure that the test results were representative of reality. The bounding nature of the test conditions virtually assured success (and in fact a far worse temperature of 150° C was also tested[6]), but post-deployment confirmation was performed by testing a used getter assembly. As expected, the two-year-old getter was hardly distinguishable from new material and KAC saw no evidence of a getter failure. Given this information, plans are currently being developed to re-use the getter material which will save time and money while providing the most efficient use of resources.

Post-Storage Activities

Storage in KAC is not the ultimate disposition for post-surveillance 3013 oxides. Another facility at SRS, the HB-Line, is responsible for the receipt of 9975s protected by hydrogen getters and dissolution of the 3013 oxides contained within. The 9975 shipping packages are transferred from KAC to HB-Line using site vehicles, opened without the need for hydrogen explosion controls, and the getter assemblies are set aside while the oxide is staged to be dissolved inside gloveboxes. HB-Line personnel survey the getter assemblies to ensure they are radiologically clean, and then they send them back to KAC for re-use.

Conclusion

Hydrogen getter technology has been shown to allow safe storage and handling of 3013 materials that produce flammable levels of hydrogen and has contributed to a great success in KAC for the interim storage of these moist Pu oxides. It allows the facility to continue vital 3013 surveillance activities and minimize the downtime associated with venting and repackaging to prevent hydrogen accumulation hazards. While the technology has been considered in recent years for nuclear waste shipping containers (itself a very promising application of getter technology), we believe that there is great potential for getters to enhance other endeavors of nuclear materials management personnel and facilities.

[5] SAND2008-5530
[6] SAND2009-8384P