This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

Using Polymeric Hydrogen Getters to Prevent Combustible Atmospheres during Interim Safe Storage of Plutonium Oxide

Todd D. Woodsmall
Nuclear Materials Storage Engineering
Washington Savannah River Company
Savannah River Site, Aiken, SC 29808

Abstract

Nuclear Materials Management (NMM) of WSRC has recently installed the capability to perform both non-destructive and destructive examination of 3013 containers of Pu oxide in accordance with DOE-STD-3013. The containers will be opened and the oxide will be sampled for analysis. The remaining bulk oxide must then be safely stored in a non-3013-compliant configuration. Available processing equipment and controls cannot prevent the oxide from adsorbing moisture during this process. Subsequent radiolysis of moisture during storage may generate combustible quantities of gases while waiting final processing, and satisfying DOE Interim Safe Storage Criteria (ISSC) would require that storage containers be vented at impractical frequencies. With support from an independent National Laboratory, WSRC/NMM has demonstrated that a commercial hydrogen getter material will effectively prevent the accumulation of combustible gas concentrations. A project overview, including storage requirements and strategies, as well as getter technology, current test results, and anticipated future developments will be addressed.

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 found 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. Across the DOE Complex, only limited surveillance examinations have been performed to date on materials packaged to the 3013 standard and stored in a non-research environment.

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 the Nuclear Materials Management (NMM) division of the Washington Savannah River Company (WSRC). Pu-bearing materials prepared and packaged in compliance with the 3013 standard from both the SRS production facilities and the Rocky Flats site have been placed into storage, but only non-intrusive (i.e. non-destructive) surveillance examinations such as exterior can inspections, digital radiography, and gamma radiation measurements have been performed. The facility at which these limited surveillances were performed has been deinventoried of all accountable nuclear material to reduce costs. NMM has recently installed the equipment necessary in KAC to perform both non-destructive (NDE) and destructive examinations (DE) as a part of surveillance. The DOE Complex sites are anticipating a wealth of knowledge about how 3013-compliant materials are behaving while in storage for several years.

Surveillance and Packaging Details

The surveillance activities include taking head gas samples, oxide samples, and cut-up pieces of the 3013 storage containers for analysis at the Savannah River National Laboratory (SRNL). After the oxide samples are sent for analysis, NMM must maintain the remaining oxide in a safe configuration, but KAC does not currently have the capability to restore compliance with the 3013 standard. For this situation, DOE has provided requirements for interim 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. NMM has developed a program to ensure that all ISSC requirements are met in the 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 SS inner can, a HEPA-filtered polyethylene bag, and a vented/filtered SS outer can. This configuration allows the multiple gas spaces to interact and become well mixed over a relatively short amount of time.

Hydrogen Hazards

One of the most significant hazards of storing Pu oxide is the generation of hydrogen formed 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 inerted. 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 additional moisture must be controlled to maintain safe storage and meet the ISSC program requirements. The ISSC program requires NMM to prevent the storage packages from containing 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, NMM 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 repackaging activities simply cannot be sustained.

Hydrogen Hazard Mitigation

In an effort to seek alternative mitigation strategies, NMM 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, it functions to catalytically recombine the elements into water at a nearly instantaneous rate, with the formed water 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. Each of these reactions is accomplished in atmospheric conditions at a wide range of temperatures with few known hindrances.

Although getter technology is not a novel concept, the use of getters for the storage of non-waste Pu oxide is believed to be a unique endeavor. Generally, polymers are strictly limited inside Pu-bearing material storage containers due to potential degradation leading to hydrogen generation, and also to concerns with neutron moderation enhancing the potential for criticality. In order to adequately 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. A perforated SS can holds the getter and molecular sieve materials and sits on top of the outer can, directly above the outermost filter, and fills the

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

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.

First, both the 3013 standard 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 use in NMM's 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 was 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. 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 during the KAC application. Second, although the getter is used by various industries at high temperatures, performance had never been quantified after continuous exposure to the temperature that NMM uses as an upper bound. Third, the getter had to remove hydrogen at a rate that would maintain the hydrogen and oxygen concentrations below the LFL. Finally, to provide a solution that would have a meaningful use in KAC, the getter would have to provide a long period of time before the facility would need to vent the storage containers.

Hydrogen Getter Testing

NMM commissioned Sandia to test each of these parameters in addition to providing technical expertise. Testing is scheduled to continue into FY 2008, and the remainder of this paper will discuss results to date and plans for future tests. 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, NMM 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 in conjunction with 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

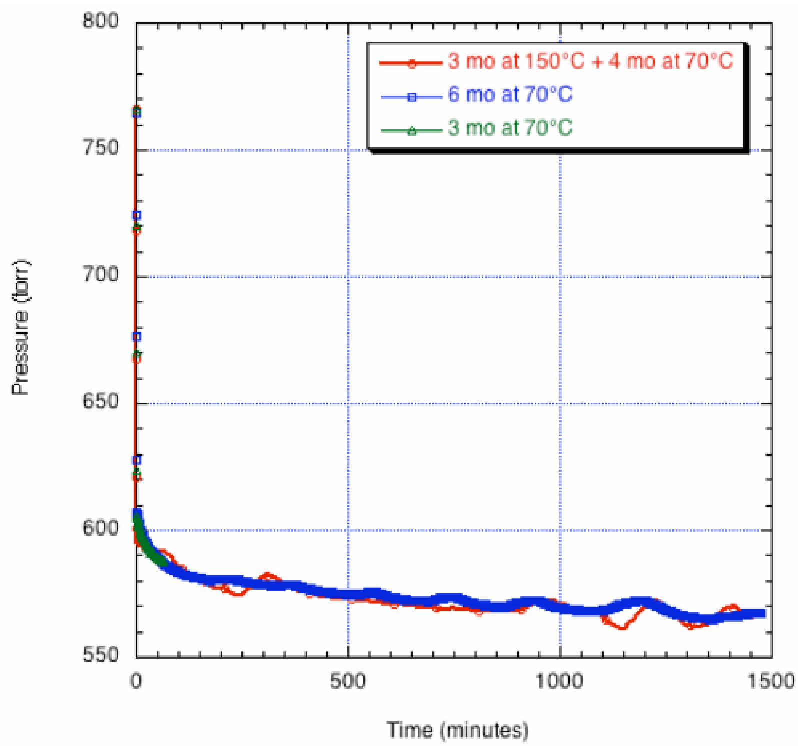
---

[2] SAND2007-0095

do not exist in the 9975 package. For example, in the test apparatus a small amount of getter was 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. NMM 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. NMM 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 as deployed. The irradiated samples were also 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 NMM 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, and 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.

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. In both cases, the additional time and temperature revealed that the getter continues to remove hydrogen both via recombination and gettering. The figure below is a data representation comparing similarities in the three series of tests. The immediate pressure drop is an artifact of the apparatus, but the evidence of hydrogen and oxygen removal is the pressure drop from about 610 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.



Future Plans

Sandia's work is ongoing. Samples of getter remain in both 70°C and 150°C ovens for use in future tests. These tests are expected to demonstrate the material's adequacy for longer term storage. NMM currently maintains a six month limit on items stored with a getter until future test results can be obtained that will allow an extension of the storage limit. Should a

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

discovery be made that the getter cannot maintain performance after a certain period of time, temperature, or irradiation, the facility will respond accordingly. Gas generation calculations have been developed to extend the storage limit beyond the getter's tested lifetime, and operational procedures are in place for safe repackaging and getter replacement efforts (to be conservative, these procedures assume an accumulation of hydrogen). After deployment, used getter assemblies will be analyzed and will either be reused or recycled as appropriate. This analysis will be performed in conjunction with Sandia, SRNL, and the getter vendor, Vacuum Energy, Inc. It is quite possible that in most cases, recombination will be the only reaction that occurs and the getter itself will have no reduction in capacity. If so, the molecular sieve that has acted as a desiccant will be replaced and the getter assembly returned for future use. If significant gettering has occurred, NMM will work with the getter vendor to reclaim as much of the catalyst as possible for the formulation of new getter.

Conclusion

Hydrogen getter technology has contributed to a great success in KAC for the interim storage of Pu oxide with varying quantities of moisture. It allows the facility to continue vital 3013 surveillance activities and minimize the downtime associated with venting and repackaging due to hydrogen accumulation hazards. While the technology has been considered in recent years for waste shipping containers, NMM believes that there are many applications possible in the shipping and storage of national interest nuclear materials and other situations where hydrogen generation is an unwanted hazard.