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New Approach to Addressing Gas Generation in Radioactive Material Packaging

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ABSTRACT

Safety Analysis Reports for Packaging (SARP) document why the transportation of radioactive material is safe in Type A(F) and Type B shipping containers. The content evaluation of certain actinide materials require that the gas generation characteristics be addressed. Most packages used to transport actinides impose extremely restrictive limits on moisture content and oxide stabilization to control or prevent flammable gas generation. These requirements prevent some users from using a shipping container even though the material to be shipped is fully compliant with the remaining content envelope including isotopic distribution. To avoid these restrictions, gas generation issues have to be addressed on a case by case basis rather than a one size fits all approach. In addition, SARP applicants and review groups may not have the knowledge and experience with actinide chemistry and other factors affecting gas generation, which facility experts in actinide material processing have obtained in the last sixty years. This paper will address a proposal to create a Gas Generation Evaluation Committee to evaluate gas generation issues associated with Safety Analysis Reports for Packaging material contents. The committee charter could include reviews of both SARP approved contents and new contents not previously evaluated in a SARP.

INTRODUCTION

Department of Energy (DOE) Operating facilities have historically used senior process personnel to address complex processing issues or repeating a processing campaign that has not been done for some time. These teams are sometimes referred to as “grey beard teams” since they often are comprised of seasoned professionals. These collections of subject mater experts (SMEs) for a variety of subjects have become more valuable not just within the individual site boundaries but across the DOE Complex.

Two such areas of expertise in which SME Teams could be utilized is for addressing gas generation from actinide material and the role actinide chemistry plays in transportation. There is an increasing body of knowledge across the Complex as the various sites have struggled with gas generation issues related to actinide processing, storage, and transportation (on and off site). There is also a growing consensus that gas generation is not an issue for pure actinide material with low activity and low moisture. A SME Team might very well be used to conclude whether gas generation is an issue for safe transportation of actinide material. It is therefore proposed that the creation of a Gas Generation Evaluation Committee to review and evaluate gas generation issues associated with the shipment of actinide material in certified Type A(F) and Type B shipping containers would be beneficial to the Package Certification Program (PCP),

DOE-NNSA Package Certification Department (PCD), and Nuclear Regulatory Commission (NRC).

Oxides of actinide materials (e.g. uranium, plutonium, neptunium) have the potential to generate gases such as hydrogen, oxygen, carbon dioxide, carbon monoxide, nitrogen, and helium just to name a few. Safe shipment requires that the total potential pressure of gases generated is within the design pressure of the package vessel. This usually includes precluding any flammable/detonable gas mixtures. The type and amount of gas generated is dependant on several factors. The most common factors that affect gas generation are: material moisture content, alpha activity, hydrogenous material (plastic) in contact with the radioactive material, impurities, and inerting. Each one of these factors could influence gas generation in a variety of ways. For example pure uranium oxide with relatively high moisture (~3 wt%) would not generate much gas because of its low alpha activity. Where as, pure plutonium oxide with a high percentage of plutonium-238 with 1wt% moisture would generate significant gas because of the plutonium-238 high alpha activity.

The safe transport of these actinide oxides between facilities across the United States is in Type B or Type A(F) shipping containers. The material authorized in a shipping container is documented in its SARP. For Type B or Type AF packages in commerce, regulatory authorities generally require the demonstration that no flammable gas is possible within the package during the shipment period .[*] As a result, packaging controls for shipping actinides in oxide form may impose extreme stabilization requirements on contents to prevent flammable gas generation from moisture or impurities.

As an example, the 9975 Shipping Package SARP[1] requires the calcination of plutonium/uranium oxide at a minimum temperature of 950 ºC for at least two hours and imposes a moisture limit of 0.5 wt %. These requirements are conservatively imposed in order to eliminate organic impurities, reduce volatile impurities, and ensure the material will not produce a flammable gas mixture even in long term storage.

Calcining at 950ºC reduces the specific surface area of plutonium/uranium oxide reducing its potential to absorb moisture. It also makes it more difficult to dissolve and process for final use and may render some items to be shipped unusable for their intended purpose. Furthermore, there is widespread experience with actinide oxides stabilized to significantly lower temperatures achieving 0.5% wt moisture and remaining stable without evolving a flammable gas mixture. Actinide oxides were shipped safely in 6M specification packages for decades without such extreme stabilization requirements, moisture controls, or impurity limits.

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[*] Standard specified in NUREG-1609, Standard Review Plan for Transportation Packages for Radioactive Material (March 31, 1999) from the Nuclear Regulatory Commission provides the following guidance: "Confirm that the application demonstrates that any combustible gases generated in the package during a period of one year do not exceed 5% (by volume) of the free gases volume in any confined region of the package. No credit should be taken for getters, catalysts, or other recombination devices."

The 9975 package imposes stabilization at this level regardless of the amount of actinide material shipped from 4.4 kg down to quantities of a few grams. Efforts are underway to allow shipment of small gram quantities (15 to 100g) of any radioactive material (with a few key exceptions) without stabilization or inerting in the 9977 Shipping Package. The goal is to also include the small gram quantity limits into the 9975 and 9978 SARPs. However this effort will not provide a transportation option which avoids high temperature calcination for materials or items above about 100 grams.

Because gas generation is dependant on a variety of material characteristics, a one size fits all approach may not be the most efficient tactic for shipping containers which are intended to be used for transporting a variety of material.

DISCUSSION

There have already been at least two occasions in the Packaging Certification Program (PCP) of DOE where a team of experts have evaluated gas generation issues associated with Safety Analysis Reports for Packaging. The first concerned shipment of Neptunium Oxide in the 9975 where a subject matter expert (SME) team was allowed by a letter amendment to make an equivalency determination without returning to the reviewer for approval. The Neptunium SME Team consisted of members with knowledge in actinide chemistry, gas generation, transportation, and the processing facilities operation. Details on this campaign are listed below. The second SME Team was formed to address gas generation issues with the shipment of plutonium oxide with a high proportion of plutonium-238 in the Radioisotope Thermoelectric Generator (RTG) Package. This SME Team, which is still active, was put in place to answer first round regulatory review question related to plutonium chemistry. The RTG SME Team consists of personnel who are considered plutonium chemistry experts within the DOE Complex.

Neptunium Oxide SME Team

In January 2007 a Letter of Amendment to the 9975 SARP neptunium oxide content requirements was approved by the DOE-EM Package Certification Program (PCP). A Neptunium Subject Matter Expert (SME) Team was formed to verify compliance with the requirements of the letter amendment. The Savannah River Site (SRS) produced neptunium oxide from two different solution sources. The first feed solution was used as the basis for the original neptunium oxide content evaluations which were incorporated into the 9975 SARP. This evaluation included gas generation testing on laboratory produced neptunium oxide from the first solution. A Letter of Amendment to the 9975 SARP was written after process upsets prevented the processing facility from meeting the original content requirements as specified in the SARP. The basis for the Letter of Amendment was the determination of the parameters which were key to gas generation. These were moisture content, alpha activity, and material purity. Also included in this Letter of Amendment was justification to allow the neptunium oxide product produced from a second feed solution to be shipped in a 9975, provided this product could be shown equivalent to the original neptunium oxide product.

Since gas generation testing could not be performed for the neptunium oxide from the second solution, a Neptunium SME Team was established to determine what parameters the second solution and oxide product had to meet. To answer this question the Neptunium SME Team determined the composition of the first material at three stages: the initial solution, the in-process solution, and the final neptunium oxide product. From these compositions the Neptunium SME Team established the criteria by which the second material would be compared to the first material. Trigger limits for impurities were established for each stage. Any impurity above the specified trigger limit had to be evaluated by the Neptunium SME Team. Provided the second material final neptunium oxide product compared favorably to the neptunium oxide product from the first material it was deemed by the Neptunium SME Team to be bounded by the gas generation testing of the first product which satisfied one of the Letter of Amendment conditions for shipment.

The initial solution and in-process solution comparisons were done to ensure that any impurities which would affect the final neptunium oxide product were removed since reprocessing the oxide was not an option. The Neptunium SME reviews of the final oxide product primarily focused on product purity, alpha activity, moisture content, and impurity results verses the trigger limits. This review was conducted for each of the neptunium oxide cans produced from the second feed solution. Although some of the neptunium oxide product cans produced from the second feed solution did occasionally exceed the impurity trigger limits, all of the cans were deemed within the original gas generation testing and acceptable for shipment. When an impurity trigger limit was exceeded the Neptunium SME Team evaluated the neptunium oxide product against the following questions:

- What was the impurity that exceeded the trigger limit?
- How much above the trigger limit was the impurity result?
- Is there an increasing or decreasing trend for the impurity results?
- What effect does the impurity have on gas generation?
- What was the neptunium assay (purity)?
- What was the alpha activity?
- What was the moisture content (level)?

After answering each of these questions, the Neptunium SME Team concluded that the neptunium oxide from the second feed solution was equivalent to the neptunium oxide produced from the first feed solution campaign with respect to the impurities and physical attributes affecting gas generation.

<u>Radioisotope Thermoelectric Generator Package SME Team</u>

In May 2009, an Addendum to the Radioisotope Thermoelectric Generator Package SARP to allow shipment of twelve plutonium oxide containers with a high proportion of plutonium-238 was resubmitted to the DOE-EM PCP for regulatory review by the Hanford Site. This addendum had previously been submitted in 2005 but received extensive questions concerning gas generation and plutonium chemistry. As a result, a SME Team was formed to address gas generation issues with the shipment of plutonium oxide with a high proportion of plutonium-238 in the Radioisotope Thermoelectric

Generator (RTG) Package. The RTG SME Team produced a white paper that addressed the regulatory review questions. This white paper was the basis for the addendum resubmittal.

The white paper addressed the material history and analytical results. The material history was important because the plutonium oxide was produced at the Savannah River Site between 1964 and 1965, stored at SRS, shipped to the Hanford Site in 1966,and stored at Hanford until present (2009). Because of good documentation, the SME Team was able to trace the materials production, shipping, and storage history through every location and evaluate the conditions that could impact the materials properties. Since the last sample of the material was taken in 1965 and taking additional samples now is not possible, the SME Team was also tasked with evaluating the materials historical sample results. The SME Team determined that the sample results were still valid because the material had been stored in controlled environments. Two of the twelve containers offered for shipment have Loss on Ignition (LOI) results greater than 1.0 wt%. LOI results are conservatively assumed to be moisture (water vapor), but could include other volatiles. The SME Team determined that the high LOI results for these two containers were influenced by gasket material that had inadvertently fallen into the containers during a repackaging evolution. The RTG SME Team white paper presented a logical argument as to why the plutonium-238 containers do not contain a flammable gas mixture.

Although it remains to be seen if the PCP review team will accept the RTG SME white paper conclusion, the use of DOE Complex experts by Hanford should help ensure the Addendum to the Radioisotope Thermoelectric Generator Package SARP is certified.

CONCLUSION

This paper proposes the creation of a Gas Generation Evaluation Committee by the DOE-EM Package Certification Program (PCP), DOE-NNSA Package Certification Department (PCD), and Nuclear Regulatory Commission (NRC) to review and evaluate gas generation issues associated with the shipment of actinide material in certified Type A(F) and Type B shipping containers. The committee's authority would be limited to determining that the material to be shipped will not generate a flammable gas mixture during or preceding shipment. Only contents compliant with the SARP in all other aspects, including radionuclide distribution, total radioactive content, impurity limits, fissile loading etc would be considered. Only issues related to content stabilization and inerting would be negotiated by the committee. Any material that could challenge the package would have to go through a full regulatory SARP review. The committee should include knowledgeable actinide chemistry, gas generation, and packaging and transportation personnel. Use of the committee would be authorized in the certificate of compliance or in the shipping containers SARP. The committee would be responsible for issuing a report that included the approval of the package Design Agency and Design Authority Engineer

[1] 9975 Safety Analysis Report, S-SARP-G-00003