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SRT-MTS-96-3026

October 17, 1996

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PHYSICAL BEHAVIOR OF PU-238 OXIDE (U)

Classification: Unclassified D. Thomas Rabun
Authorized Derivative Classifier

Summary

More than 15,000 drums containing solid waste contaminated with Pu-238 oxide are stored at the Savannah River Site (SRS). This waste resulted from processing Pu-238 at SRS, Mound, and Los Alamos. Vitrification technologies are being evaluated as a means to reduce the volume of this waste and to convert it into a form which can be transported and stored more safely.

Several unusual physical behavioral characteristics of Pu-238 oxide powder were apparent as this material was processed. This report describes the physical properties of Pu-238 oxide, provides an explanation for the differences in the behavior of Pu-238 and Pu-239, and predicts the implications of these properties on the partitioning behavior of Pu-238 oxide during vitrification. The requirements of Milestone B1 in TTP No. SR1-7-MW-51, Rev. 2, are satisfied by this report.

Process History

Several facilities were involved in the Pu-238 program. The Pu-238 isotope was produced in SRS reactors and separated in the HB-Line canyon building. The oxide was first fabricated into fuel pellets at Mound Laboratories and later in the Plutonium Fuel Fabrication (PuFF) facility at Savannah River. The fuel was most recently fabricated at Los Alamos National Laboratory (LANL). An analytical support laboratory was also operated by SRS to support the Pu-238 program. The Savannah River Technology Center (SRTC) supported these production operations in several smaller laboratory facilities.

An understanding of the fuel pellet fabrication process is necessary to understand the nature of the contaminated waste which resulted from the process. At Mound, fine hydroxide particles were precipitated in gelatin-like cakes. After calcination, the cakes were calcined and broken up into granules which generated some fines. The SRS separations process produced plutonium oxalate. Calcination of the oxalate produced oxide powders with an average particle size of five to ten microns. The particle size of these powders was further reduced by ball-milling for 12 to 32 hours. This created very fine particles with an average size of less than two microns and a significant fraction in the submicron range. Nearly all of the Pu-238 oxide at SRS and Los Alamos was ground to this size range.

Each time the ball mill jars were opened or the material was transferred another container, a cloud of fine particles of Pu-238 oxide particles was released into the glove boxes or shielded cells. The granulation process, which involved mechanically rolling a cold-pressed compact through a series of sieves, also generated fines. The granules were sintered and then mixed by tumbling in a jar without grinding media. This mixing process generated additional fines. Fuel pellets were formed by hot pressing. Some of the pellets were analyzed by metallography on mounted sections. Sectioning, grinding, and polishing operations also generated fines.

Since the glove boxes and hot cells for the fabrication were all interconnected, the fine particles were free to migrate throughout the entire production line. All materials within the glove boxes and hot cells were eventually coated with a layer of fine Pu-238 oxide particles. Many of these fine particles were collected on the HEPA filters in the exhaust systems. Therefore, all of the waste materials removed from the glove boxes and hot cells is expected to be coated with a layer of very fine Pu-238 oxide particles.

The Pu-238 program has created large quantities of non-homogeneous debris solid waste. This waste contains large quantities of organic materials including rubber, polyethylene, polyvinyl chloride, paper, and wood. Iron based metals, aluminum, copper, brass, and even some refractory metals were discarded as waste. This waste stream also includes ceramics and high density graphite.

A disproportionately high number of safety incidents were related to Pu-238 contamination at Savannah River compared to Pu-239. Pu-238 is regarded as the most hazardous material processed on site. Approximately 100 to 150 times as much Pu-239 was processed as Pu-238. Reportable incidents involving contamination from these isotopes were maintained in databases. A search of the databases (Ref. SRS Fault Tree Data Banks) indicates that there were 658 reportable contamination incidents involving Pu-238 and 185 incidents involving Pu-239. Hence, there were 3.5 times as many incidents related to Pu-238 despite processing more than one hundred times as much Pu-239. This data supports the conclusion that Pu-238 is much more difficult to contain than Pu-239.

Physical Properties

Personnel involved in the processing of Pu-238 have observed many unusual characteristics of the oxide. In many cases the oxide contamination appears to exhibit lifelike characteristics as it "flies" through the air or "walks" along pipes. In some cases, the fine particles appear to behave more like a gas than a solid.

Pu-238 is used as a heat source in Radioisotopic Thermal Generators (RTGs) because it produces about 0.5 W (thermal power)/gram by emitting alpha particles. In RTGs, Pu-238 fuel pellets encased in graphite blocks are stacked in arrays to produce temperatures exceeding 1000°C to supply the required power. The temperature of small particles has not been measured experimentally but is obviously high enough to burn through rubber.

The alpha decay and heat caused numerous failures of 35 mil thick rubber gloves, sometimes in a matter of days. Several types of rubber were tested but none were very effective in containing Pu-238. Frequent glove changes, as often as weekly, were performed to minimize the number of glove failures. Contamination incidents were also associated with glove changes, material transfers, and waste removal.

Once the Pu-238 oxide escaped containment, the particles sometimes traveled for hundreds of feet rather than settling directly to the floor. Based on Stoke's Law, the settling time is inversely proportional to the diameter squared. The settling time for Pu-238 oxide particles in static air from a height of four feet is 36 seconds for a 10 micron particle, 1 hour for a 1 micron particle, and 4 days for a 0.1 micron particle. The fine particles create an aerosol which travels with the air currents throughout the lab. The particles often contaminate surfaces at elevated levels, around corners, and hundreds of feet away from the original source of the contamination. Other types of radioactive materials do not appear to be nearly as mobile as Pu-238 and are usually spread by physically spreading the materials from one surface to another.

It has also become apparent that Pu-238 contamination is more easily dispersed from surfaces than other types of contamination. This tends to make Pu-238 decontamination more difficult as the particles migrate to other surfaces, including those which have already been decontaminated. The fine particles are easily dispersed into the air, often recontaminating surfaces after several hours or even days.

Pu-238 vs. Pu-239

The chemical properties of Pu-238 and Pu-239 oxides are identical. In fact, Pu-239 was used as a simulant to develop Pu-238 chemical precipitation processes at SRS. The density and mechanical properties of the oxides are also equivalent.

The key to the difference in the behavior of Pu-238 and Pu-239 is due to the difference in the radioactive properties of the isotopes. The activity of Pu-238 is nearly 300 times greater than that of Pu-239. As discussed earlier, the high alpha decay creates a significant self-heating effect in Pu-238. Because the fine particles of Pu-238 oxide are thermally hot, they do not absorb water.

The unusual behavior of Pu-238 oxides can be attributed to its tendency to remain as individual particles. Fine powders normally have a strong tendency to form agglomerates. Agglomerates are weakly bonded clumps of particles. Agglomerates behave similarly to large particles and settle rapidly in air or liquids.

The most common cause of agglomeration is by adsorption of water vapor from the air. Since a vapor is best adsorbed or condensed at contact points, fine powders with many contact points per unit of mass are more sensitive to humidity than coarse particles. The hydrogen bonding interaction of polar water with the surface of the particles is an important factor in the adhesion of particles exposed to water vapor.

Hydrophobic grinding aids are used when dry grinding most oxides to prevent water from wetting the particles and causing agglomeration. Below 10 microns, agglomeration is a key problem and without aids most of the energy of grinding goes into breaking up agglomerates. Pu-238 oxide was dry milled to an average particle size of less than two microns without any grinding aids and agglomeration was not a problem. The Pu-238 self-heating obviously prevented the adsorption of water on the surface of particles and, therefore, the fine particles of Pu-238 oxide did not form agglomerates.

There are other attractive forces such as dipoles and static charges between particles which can cause agglomeration. These forces are difficult to quantify but relatively weak compared to water adhesion. Most of the alpha decay energy from Pu-238 is transformed into heat as the alpha particles move through the matrix. However, alpha emissions from the surface of Pu-238 particles may have enough energy (~5.5 Mev) sufficient to overcome these weak attractions. Therefore, alpha emissions from the surface of small particles may also be responsible for breaking up agglomerates.

As fine particles of Pu-238 eventually contact a surface, the particles are likely to adhere to the surface if it contains a layer of adsorbed water. However, if the self-heating effect is sufficient to dissipate the water layer in the contact areas, the particles will be easily dispersed. This accounts for the behavior of Pu-238 observed during decontamination efforts.

Pu-238 particles in contact with plastics may actually burn into the plastic. This effect will temporarily fix the contamination and should help to reduce partitioning to the off-gas in the melter system.

Discussion

Partitioning refers to the dispersion of the radioisotopes throughout the melter and into the off-gas system. Partioning is an important factor in the selection of the melter technology. As radioisotopes are dispersed through the melter and into the off-gas system, radiation and contamination levels will increase in the transfer lines and components of the off-gas system. This increases the radiation exposure and risk associated with the operation and maintenance of the melter.

It is expected that turbulence within the melter will increase the quantity of radioisotopes which escape capture in the melt. Turbulence is created by the addition of waste, suction to the off-gas system, combustion, and the arcs between the electrodes and melt.

Based on the difficulties encountered in containing Pu-238 during processing, it is expected that similar difficulties will be encountered during waste processing. The fine particles of plutonium-238 oxide

are expected to be particularly difficult to capture in the melt. As discussed earlier, these very fine particles are easily dispersed from surfaces. The fine Pu-238 oxide particles which escape entrapment in the melt during feeding or combustion are likely to be exhausted into the off-gas system of the melter.

Therefore, it is anticipated that significant quantities of radioisotopes will be dispersed throughout the melter and into the off-gas system. It may be possible to minimize the partitioning of radioisotopes by temporarily fixing contamination on the waste with a water mist or by controlling process parameters and turbulence in the melter. Partitioning experiments with plutonium-238 oxide contamination on waste compositions which closely simulate the characteristics and contamination levels of the actual waste are needed to fully evaluate this potential problem.

Although bench-scale experiments cannot provide a complete demonstration of the technology, they can provide data and experience needed to scale-up the process. Partitioning experiments could provide a basis for calculating shielding requirements for the melter and off-gas treatment system. Corrosion in the melter and off-gas system is also a concern. Pu-238 is likely to accelerate corrosion rates of metals in the off-gas system.

Conclusions

The unique physical behavior of Pu-238 oxide cannot be simulated by other oxides, even by Pu-239 oxide. Pu-238 self-heating prevents water adsorption on the surface of particles. This lack of surface water, and perhaps alpha emissions from the surface of the particles, prevents the formation of agglomerates.

The Pu-238 production process produced fine oxide particles which tend to remain as fine particles. These particles are easily dispersed from surfaces and behave as an aerosol. This behavior has been observed during processing and is expected to be a factor in the partitioning of Pu-238 when the waste is processed in a high temperature melter.

It may be possible to minimize Pu-238 partitioning to the off-gas system by controlling process conditions, particularly those which cause turbulence above the melt. Additives may be required to promote agglomeration of the fine particles. The burn-in of Pu-238 contamination on organic materials should also be evaluated for possible beneficial effects on partitioning.

Sincerely,

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