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Characterization of Representative Materials in Support of Safe, Long Term Storage of Surplus Plutonium in DOE-STD-3013 Containers

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Institute for Nuclear Materials Management, 51st Annual Meeting, July 11-15, 2010, Baltimore, MD

Abstract

The Surveillance and Monitoring Program (SMP) is a joint LANL/SRS effort funded by DOE/EM to provide the technical basis for the safe, long-term storage (up to 50 years) of over 6 metric tons of plutonium stored in over 5000 DOE-STD-3013 [1] containers at various facilities around the DOE complex. The majority of this material is plutonium that is surplus to the nuclear weapons program, and much of it is destined for conversion to mixed oxide fuel for use in US nuclear power plants. The form of the plutonium ranges from relatively pure metal and oxide to very impure oxide. The performance of the 3013 containers has been shown to depend on moisture content and on the levels, types and chemical forms of the impurities. The oxide materials that present the greatest challenge to the storage container are those that contain chloride salts. The chlorides (NaCl, KCl, $CaCl_2$, and $MgCl_2$) range from less than half of the impurities present to nearly all the impurities. Other common impurities include oxides and other compounds of calcium, magnesium, iron, and nickel. Over the past 15 years the program has collected a large body of experimental data on over 60 samples of plutonium chosen to represent the broader population of materials in storage. This paper will summarize the characterization data, including the origin and process history, particle size, surface area, density, calorimetry, chemical analysis, moisture analysis, prompt gamma, gas generation and corrosion behavior.

Introduction

The Material Identification and Surveillance (MIS) Program (a sub element of the overall SMP) at Los Alamos National Laboratory is charged with characterizing and evaluating nuclear materials in long term storage per the DOE-STD-3013 Standard, and provides technical support to the processing sites to assist in the resolution of problems that develop during stabilization and packaging activities. Section 6.6 of the Standard provides for this activity: "As a part of site Quality Assurance Plans, the sites are responsible for assuring that materials being packaged to this Standard are represented by the items accumulated in the Materials Identification and Surveillance Program." The MIS Program is guided by a working group consisting of Department of Energy (DOE) officials and DOE contractors including Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), Rocky Flats Environmental Technology Site (RFETS), Hanford Site, and Savannah River Site (SRS). The MIS characterization and evaluation activity began in earnest in 1997 with receipt of the first items from existing inventory at LANL, and subsequently Rocky Flats and Hanford. These MIS samples are full-size representations of items planned for long-term storage and were selected by individual site representatives for characterization and analysis in the program. This paper is an update to a 1999 characterization status report [2], and focuses on the data gathered over the last eight years by the stabilization and characterization component of the MIS Program. This characterization data is an essential element of the technical basis for the safe, long-term storage of over 6 metric tons of plutonium in ~5000 containers stored across the DOE complex.

Material Representation and Sampling

The MIS Program has collected 65 unique items for representation in the MIS inventory as described in Table 1, and some example photographs are illustrated in Figure 1 [3]. These photographs illustrate the large variety of materials that are stored in 3013 containers and the bulk effects of processing

(calcination and milling). For the purposes of this report the material has been categorized by the originating process type (Process Category), by whether the material is the primary product or a byproduct of the process (Process Subcategory), and by the site of origin (Source Site). The samples in the MIS program were provided by Rocky Flats, Hanford, and LANL. The absence of samples from LLNL and SRS stems from the fact that these sites were able to represent their inventories with samples that originated from RFETS, Hanford or LANL. The containers packaged by SRS were linked to representative samples based on the processing history of the material, and the containers packaged by LLNL were linked to representative samples based on the prompt gamma characterization [4].

Table 1. Summary of the MIS inventory of samples representing the broader inventory of plutonium in long term storage

Process Category	Process Subcategory	Source Site	Number of MIS Samples	Min Pu%	Max Pu%	Min U%	Max U%
Aqueous Processing	Byproduct Oxide	Hanford	3	29	65.6	0	0
		RFETS	7	7.7	85.9	0	0.5
	Product Quality Oxide	Hanford	2	85.2	87.5	0	0
		LANL	8	76.6	87.8	0	0
		RFETS	2	84.2	84.5	0	0
Metal Oxidation	Byproduct Oxide	Hanford	1	86.3	86.3	0	0
		RFETS	2	19.6	69.8	0	0
	Product Quality Oxide	RFETS	5	77.7	87	0	0
Miscellaneous Oxides	Miscellaneous Oxide	Hanford	1	83.4	83.4	0	0
		LANL	3	66.8	77.5	0	0
Mixed Actinide Operations	Byproduct Oxide	Hanford	1	13.4	13.4	65.1	65.1
		LANL	1	36.1	36.1	14.7	14.7
		RFETS	4	13.8	81.6	2.3	69.2
	Miscellaneous Oxide	LANL	8	0	84.6	0	84.3
	Product Quality Oxide	LANL	3	4.9	17.5	70	81.6
		RFETS	1	85.1	85.1	0.1	0.1
Molten Salt Operations	Byproduct Oxide	Hanford	6	32.7	70.9	0	0
		LANL	2	71.9	74.2	0	0
		RFETS	6	33.7	77.7	0	0

Aqueous Processing

The packaged materials in this process category include product quality oxides produced at Hanford, LANL, and Rocky Flats and the byproducts from these processes. The product quality oxides include mostly pure materials produced in the oxalate precipitation (used by Hanford and LANL) and peroxide precipitation (used by Rocky Flats) processes. The byproducts from these uranium and plutonium recovery processes include dissolution residues (heels that could not be dissolved) from processing foundry and scrap oxide in the oxide dissolution process and oxides from the magnesium hydroxide precipitation process. The packaged materials are represented by 22 samples from three sites. The samples include 12 product quality oxides with 76.6 % to 87.8 % Pu. and 10 byproduct oxides with 7.7 to 85.9 % Pu. Fluorides were introduced as reagents in the dissolution process and are common in the dissolution residues. Small amounts may be also present in the product oxide depending on the degree to which it was purified after precipitation. Oxide from the magnesium hydroxide precipitation process is considered byproduct oxide because of the low actinide content.

Metal Oxidation

The packaged materials in this process category include product quality oxides and impure oxides produced by burning pure and impure metal (buttons, ingots, turnings) to oxide, metal brushings, casting skulls, and sweepings. The quality of the oxide depends on the source material. The packaged materials are represented by 8 samples from the three sites. Five samples are product quality oxides from Rocky

Flats with 77.7 to 87 % Pu, and the three samples are byproduct oxides from Hanford and Rocky Flats with 19.6 to 86.3 % Pu. The major impurities of byproduct oxides generally include chloride salts.

Mixed Actinide Operations

The packaged materials in this process category include product and byproduct Pu and Pu/U mixed oxides from the fabrication of mixed oxide reactor fuel, mixed oxides from research and development

Metal Oxidation Product, Rocky Flats, 011608 (As Received)

Aqueous Processing Product Quality Oxide, Hanford, BLO-39-11-14-0041 (As Received)

Molten Salt Operations Byproduct Oxide, Hanford, ARF-102-85-295 (As Received)

Molten Salt Operations Byproduct Oxide, Hanford, ARF-102-85-295 (After Calcination)

Aqueous processing Byproduct Oxide, Rocky Flats, 07242201A (As Received)

Aqueous processing Byproduct Oxide, Rocky Flats, 07242201A (After Rod-milling)

Figure 1. Photographs of materials received from Hanford and Rocky Flats for characterization

operations and impure scrap resulting from glovebox cleanout. Also included in this group is high purity mixed oxide recovered from polycubes produced at Hanford. The packaged materials are represented by 18 samples from three sites. The four product quality oxides are from LANL and Rocky Flats, and have 84.5 % to 87.5 % Pu+U. The six byproduct oxides are from Hanford, LANL and Rocky Flats, and have 50.8 to 83.9 % Pu+U. This category also includes 8 miscellaneous mixed Pu/U oxides from LANL with 0-86.7% Pu and from 0 to 84.3 % U.

Molten Salt Operations

The packaged materials in this process category include byproduct oxides from pyrochemical processing at Rocky Flats and LANL. Most of the material packaged to date originated at Rocky Flats and consists of electrorefining scrape-out material and foundry oxide, high in chloride salt impurities. This chlorinated oxide accumulated at Rocky Flats, and a portion was transferred to Hanford, LANL, and Savanna River Site (SRS) for recovery. Most of that material was never recovered, however, and it remained at these sites until it was eventually packaged in 3013 containers for long-term storage. The packaged materials are represented by 14 samples received from Hanford, LANL and Rocky Flats 32.7 % to 77.7 % Pu.

Miscellaneous Oxides

A number of packaged oxides do not fall into any particular group. The materials consist of sources, standards, oxide from R&D operations, sludges, and sweepings from a variety of processes. The packaged materials are represented by 4 samples from two sites. One sample originated in the Hanford direct denitration process and contains 83.4 % Pu. Three samples are from LANL and have 66.8 to 77.5 % Pu. Two of these samples are plutonium fluoride standards (PuF4-1 and YBG2-NRDL-4), and one is a mixture of materials from various processes at Rocky Flats.

Sample Preparation

The typical processing path followed by MIS samples received at LANL is shown in Figure 2. The samples were first selected by packaging sites based on a materials representation plan approved by the MIS Working Group. The receiving site performed required nuclear materials accountability receipt verifications once an item was received, which included gamma-ray spectrometry and calorimetry, and in some cases the items were radiographed. The items were then transferred to the unpackaging glovebox where they were logged in, assigned tracking codes, visually inspected for damage, weighed, photographed, and opened. Once open, the contents of each container were inspected and photographed. Early in the program, items were sent for can puncture and gas sampling [2]. Based on resource constraints, later items were not gas sampled. Approximately nine different samples were pulled from each parent from among the fines and chunks after sieving through a 40 mesh screen and V-blending for one hour. The balance of the material was placed into a ceramic calcination boat for subsequent stabilization at 600-950°C.

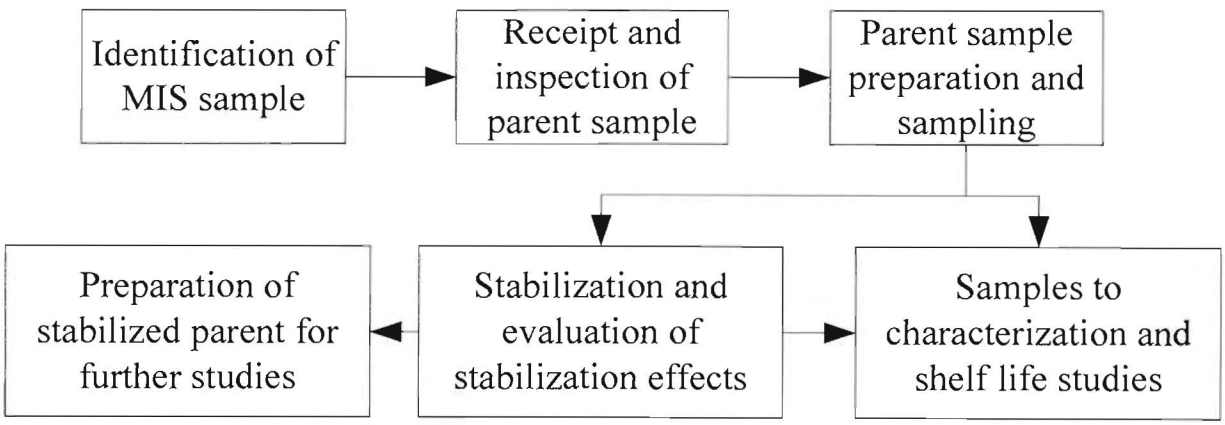

Figure 2. Sample preparation and processing path for MIS samples

Calcination

Each MIS parent item was stabilized at 950°C for a minimum of 2 hours. To examine the effects of calcination temperature upon stabilization, some parent items were split and a portion was stabilized at a lower temperature (600°C for 12 hours or 800°C for 1 hour) prior to the 950°C stabilization. This was done for materials received from Rocky Flats. In addition, some materials (e.g., from Hanford) were sequentially stabilized, first at 600 or 800°C, then at 950°C.

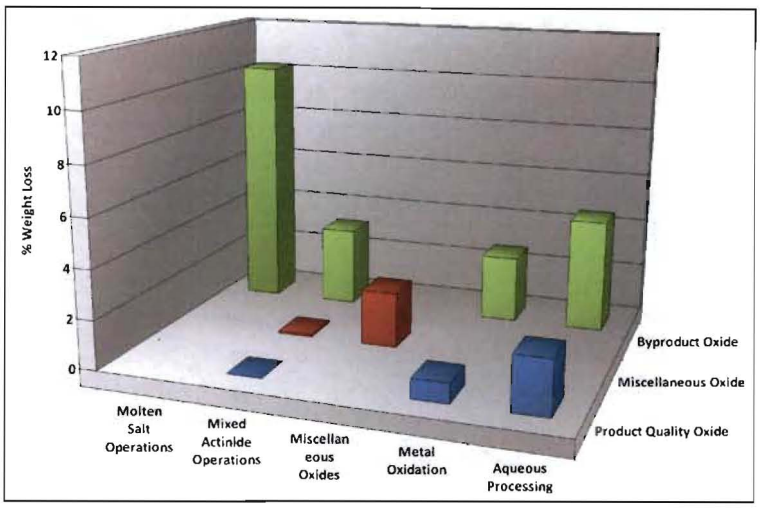

Figure 3. Sample weight loss after calcination at 950°C

The weight lost upon calcination of the samples varies significantly depending on the level of moisture and other impurities. The average percent weight loss after calcination at 950°C is illustrated in Figure 3. As expected, the byproduct oxides lose significantly more weight than the product quality oxides. Also, the byproduct oxides from aqueous processing and molten salt operations tend to lose significantly more weight than the byproducts from metal oxidation and mixed actinide operations. The high weight losses seen at higher temperatures for the pyrochemical residues are mostly attributed to loss of chloride salts.

Characterization

The parent material were sampled for the following analyses:

- Particle size
- Surface area
- Density
  - Particle density (Pycnometer)
  - Bulk and tap density
- Calorimetry
- Moisture, by LOI, TGA, IGA, or SFE
- Analytical chemistry
- X-ray diffraction
- X-ray fluorescence and
- Shelf-life surveillance

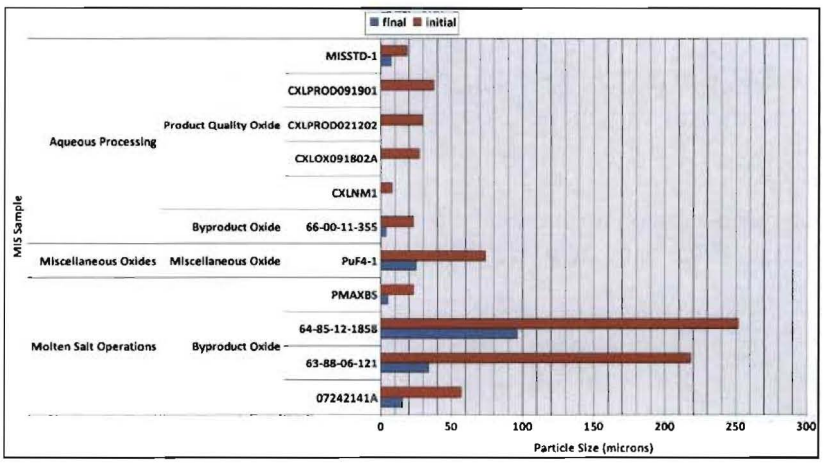

Figure 4. Initial and final average particle size measurements of MIS samples after sonication

Particle Size

The results in Figure 4 give the average particle size for several MIS samples. The plutonium oxide particles are typically on the order of 10's of microns when produced in aqueous processes. The large particle size of the samples from molten salt operations suggests that small plutonium oxide particles are held together by salts and possibly other insoluble impurities. Particle size measurements were made on several pure and impure MIS samples before and after stabilization. Measurements were

made using either the laser diffraction (LD) technique with a Horiba LA-920 particle analyzer or by using the electronic sensing zone (ESZ) technique with a Beckman Coulter Multisizer 3 analyzer. Both techniques require a small amount (~100 mg) of riffled sample to be suspended in a flowing electrolyte solution (ISOTON 3). The results show that the size of the suspended particles decreases with sonication time as the insoluble plutonium oxide particles become separated from the soluble material (usually chloride salts). Therefore, the initial results give the size of the salt-coated particles, and the final results give the size of the plutonium oxide particles.

Surface Area

Surface area influences chemical reactivity and moisture absorption behavior (see Figure 5). Materials with a high surface area are a packaging concern because they have the greatest potential to adsorb moisture. Calcination at 950°C has been shown to reduce the surface area and thereby decrease the potential for moisture absorption. Therefore, surface area measurements were obtained on the MIS samples before and after high temperature stabilization. The measurements were obtained using the Quantachrome NOVA 3000 instrument, which uses a gas sorption technique which is widely recognized as the preferred method becasue surface area is proportional to surface roughness, and gas sorption allows full contact with the entire surface. Samples are first heated under a vacuum to ensure that the surfaces are free of water and other contaminants. The temperature is then lowered and nitrogen gas is injected into the sample holder and allowed to absorb onto the surface. Temperature and pressure are then adjusted to allow a single layer of nitrogen molecules to be adsorbed over the entire surface. The amount of gas adsorbed is recorded and these data are then used to solve the B.E.T. equation for surface area.

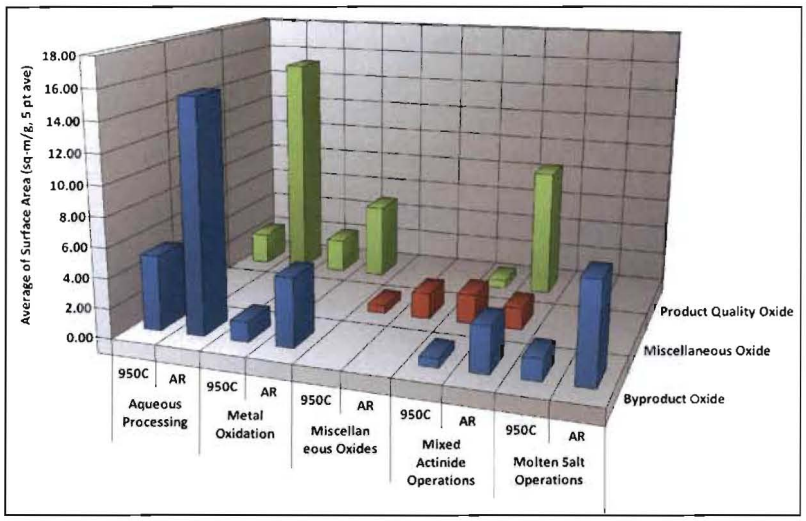

Figure 5. Average surface area measurements for materials before (AR) and after calcination (950°C) arranged by process categories

Density

Bulk density, tap density, and particle density measurements were obtained for the MIS samples (see Figure 6). Each technique provides different information about the material. Bulk density measurements are used to give the volume occupied by a given mass of material. These measurements are useful for estimating the appropriate number of containers necessary for packaging

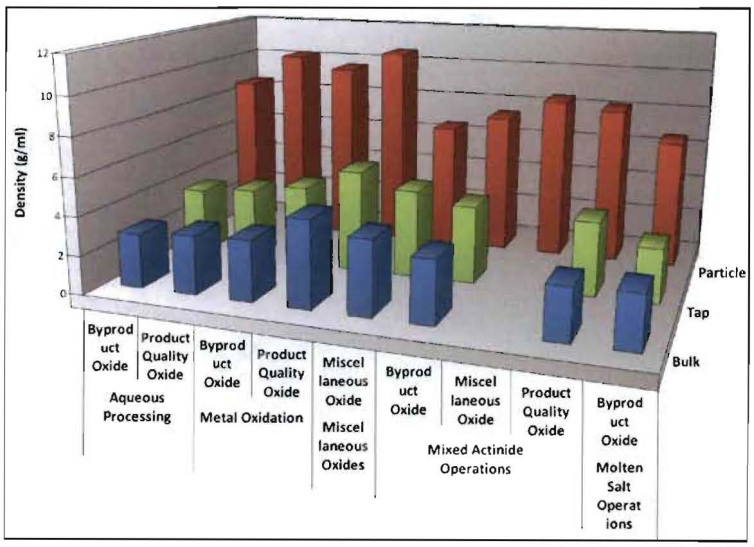

Figure 6. Average density measurements for various materials calcined at 950°C

material. Bulk density measurements are made by pouring material into a pre-weighed graduated cylinder. The volume of the material and the weight of the full cylinder are then recorded. Tap density measurements show how the material can be compacted. These measurements are then made by placing the pre-weighed graduated cylinder on an instrument known as an Autotap and tapping the cylinder in an up and down motion for a predetermined number of "taps". The volume of material after completion of this process is then used to determine the tap density. The particle density or pycnometer density gives the density of the individual particles that comprise the bulk material. This measurement is used to calculate the free volume inside a container. Particle density is determined using helium displacement pycnometry using a Quantachrome Stereopyc instrument, together with a standard laboratory analytical balance. The difference between the high pycnometer particle densities and the low bulk/tap densities reveals that the void volume in the containers can be quite large.

Calorimetry

Calorimetry and gamma-ray spectrometry were used to determine the wattage (see Figure 7), mass of plutonium and other actinides, and the plutonium isotopic composition for each MIS Item. These parameters are used to determine purity of the plutonium (and actinide) content of the material and to show whether the plutonium is weapons grade, fuels grade, or reactor grade. The measurements were required for each plutonium-bearing item upon receipt at Los Alamos to update the Materials Accountability Safeguards System (MASS). Any differences in the amounts of Pu measured prior to and after the shipment to Los Alamos were reconciled before any processing could begin. Gamma-ray spectra up to 1 MeV were obtained for each sample with a nominal 20% efficiency coaxial HPGe detector. The gamma ray spectra and the wattage were loaded into the FRAM Gamma Ray Isotopic Analysis software (v 4.2) that calculates the isotopic composition and mass of plutonium and other

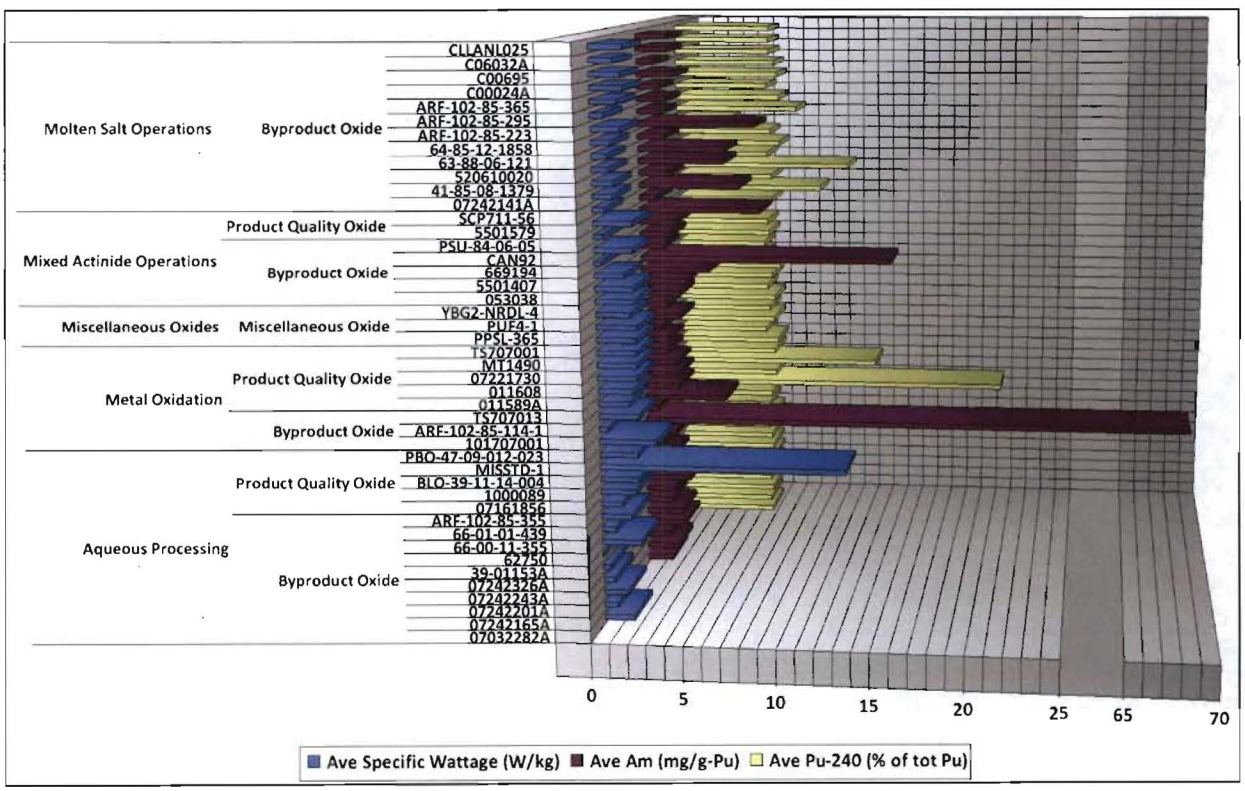

Figure 7. Average specific wattage (W/Kg), americium (mg/g-Pu) and Pu-240 (% of tot Pu) concentrations for a variety of samples before calcination

actinides. The other spectrum was obtained in the high-energy region (up to 5 MeV) of the gamma-ray spectrum for prompt gamma-ray analyses.

Table 2. Prompt gamma detection capability ($LLD_{60\ min}$ = lower limit of detection for 60-minute count)

Element	$LLD_{60\ min}$ (ppm)	Semiquantitative
Li	300	No
Be	100	Yes
B	500	No
O	130,000	No
F	2,000	Yes
Na	200	Yes
Mg	600	Yes
Al	2,000	Yes
Si	Not available	No
P	8,000	No
Cl	6,400	Yes
K	20,000	Yes

Prompt Gamma

Prompt gamma (PG) analysis is a nondestructive, nuclear, elemental analysis technique that uses charged particle reactions to activate and interrogate a sample. In this technique, certain light elements present in the plutonium oxide sample matrix are identified through the characteristic gamma rays that are emitted during or following nuclear activation with alpha-particles emitted from the plutonium. Using this technique, we can detect 12 light elements and obtain semi-quantitative estimates of concentration for 7 of these elements. The elements sensitive to PG analysis are given in Table 2 along with the lower limit of detection for a 60-minute count ($LLD_{60\ min}$) in parts per million (ppm).

Prompt gamma measurements are obtained by counting containers with a nominal 20% efficiency coaxial HPGe detector and obtaining a gamma-ray spectrum in the range 0 to 5 MeV. The gamma-ray spectra are analyzed with the LANL-developed Prompt Gamma Analysis Software v. 4.7 that uses calibration curves to estimate the impurity concentration based on the normalized peak areas. Count rates are normalized to the total alpha activity of Pu and Am.The calibration curves used in this method were developed using analytical chemistry and PG measurements on MIS materials. The calibration curves were then used to estimate the concentrations of the impurities in the packaged materials, most of which do not have analytical chemistry measurements. Therefore, PG analysis provides the only record of the impurities present in these materials. Certain impurities such as chloride salts are of concern for long-term storage, as they may increase the risk of container degradation over time, and many of these elements can be detected and their concentration can be determined on a semi-quantitative basis using PG analysis. The average values of some impurities measured by PG are illustrated in Figure 8.

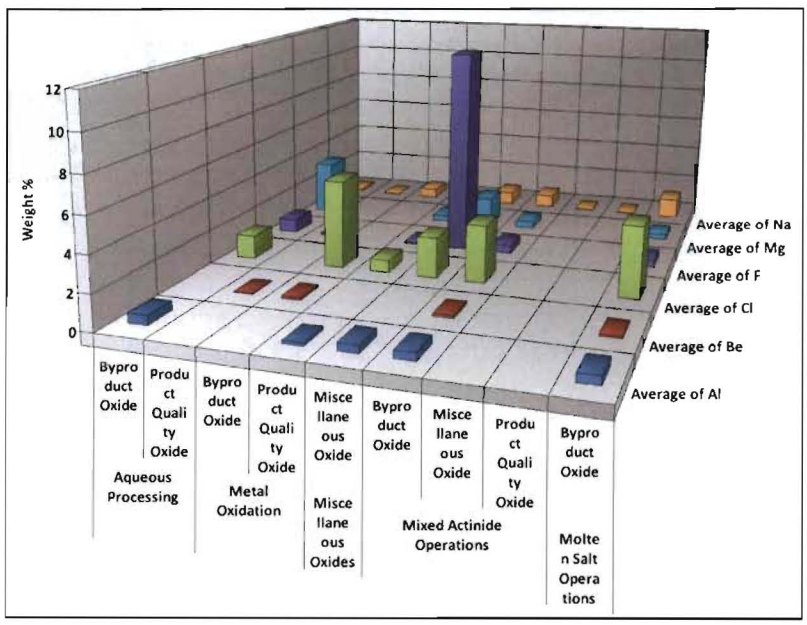

Figure 8. Estimated impurity levels measured by prompt gamma spectroscopy

Other Characterization

Additional characterization results are beyond the scope of

this paper, but are planned for publication as a LANL permalink [3], including moisture measurements, analytical chemistry, X-ray diffraction, X-ray fluorescence, and shelf-life surveillance data and analysis.

Summary

This report provides an overview of the results of the comprehensive characterization studies that have been performed on the plutonium samples used to represent the metric ton quantities of similar materials that are currently stored in 3013 containers across the DOE complex. This information is a key element of the technical basis for understanding the behavior of plutonium in the presence of a wide variety of impurities over long periods of time. The broader significance of this work is that it provides the technical underpinnings for major programs with national and international implications (e.g., the Mixed Oxide Fuel, CMRR, etc.) that depend on the need to safely store various forms of plutonium, and it provides detailed information on a broad cross-section of plutonium materials that likely represents a bounding case for material contents in storage across the DOE complex.

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1. Energy, U. S. DOE (2004), "Stabilization, Packaging, and Storage of Plutonium-Bearing Materials" DOE-STD-3013-2004.
2. Mason, R. E., Allen, T. H. et al., (1999) "Materials Characterization and Surveillance: June 1999 Characterization Status Report" LA-UR-99-3053
3. A significant portion of the characterization data in this paper is available on the LANL permalink web site. For details refer to Table 2 and reference #12 in the following publication: Duffey, J. M., Veirs, D. K., Berg, J. M., Livingston, R. R. "Pressure Development in Sealed Containers with Plutonium-bearing Materials" *Journal of Nuclear Materials Management*, Spring, 2010, Volume XXXVIII, No. 3. A more detailed version of this report (with item level detail) is planned for publication at the same permalink.
4. Narlesky, J. E., Peppers, L. G., Friday, G. P. (2009), "Complex-Wide Representation of Material Packaged in 3013 Containers" LA-14396.