Preparing Plutonium for Shipment and Long-Term Storage

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ABSTRACT

The Materials Identification and Surveillance Program at the Los Alamos National Laboratory was created in response to DNFSB (Defense Nuclear Facility Safety Board) recommendations to establish parameters for safe storage of plutonium-bearing materials destined for DOE materials disposition in accordance with DOE standard 3013 (DOE-STD-3013-99)[1]. The excess plutonium at the Los Alamos National Laboratory is now in the queue for disposition. However, since routine shipments of plutonium have not occurred throughout the complex for several years, new regulations and guidance must be satisfied. This paper describes the status of the material preparation for shipment as well as some of the issues to be resolved at Los Alamos in order for material to meet final disposition criteria.

INTRODUCTION and BACKGROUND

In support of Cold War efforts, the Los Alamos National Laboratory (LANL) supplied pure plutonium metal to Rocky Flats and other sites throughout the DOE complex. Once the Cold War ended excess weapons grade plutonium must be safely stored at DOE facilities until final disposition. The Defense Nuclear Facilities Safety Board (DNFSB) recommended that complex-wide programs be established to stabilize all plutonium-bearing materials as a preparation step for long-term storage. The current plan is to store this excess material in specially designed containers for the next 50 years. Potential difficulties associated with plutonium oxide storage arise primarily from a combination of its chemical properties, physical properties, and impurities. The Materials Identification and Surveillance (MIS) program, which directs the work contained in this document, was established by LANL to characterize materials from each of the sites prior to packaging in sealed containers. Only two failure mechanisms for these containers have currently been identified. The two mechanisms are over pressurization and corrosion.[2] These mechanisms are assisted by the presence of water, leading to the prudent approach of thermally desorbing reactive species from the oxide and restricting readsorption prior to sealing in the specially designed container.

DOE Standard 3013-99 “Stabilization, Packaging, and Storage of Plutonium-Bearing Materials” was developed to “provide criteria for stabilization of plutonium-bearing materials at DOE facilities to safe and stable forms that can be packaged and placed in storage with minimal surveillance for up to 50 years.”[1] The 3013 Standard contains numerous criteria, including a description of the stabilized material (i.e. plutonium-bearing metals and oxides containing at least 30 wt.% plutonium plus uranium) stabilizing conditions, stabilization testing (as evidenced by the moisture content, specifically for oxides), descriptions of the packaging container assembly, container construction, fill gas, mass of contained materials, as well as the prescribed surveillance program to ensure that the stored plutonium-bearing materials continue to be stored safely until the material reaches its final disposition.

This paper will describe some of the information discovered to-date regarding only one aspect of the standard described above: moisture uptake of plutonium-bearing oxides after stabilization. DOE-STD-3013, Section 6.1, states that stabilized materials will meet a moisture limit of 0.5 weight percent or less at the time of packaging.[1] Compliance with this requirement in the standard is not a straight forward achievement, either in the stabilization of the material itself, or in determining the moisture content of plutonium-bearing oxides, both in their original (here-after called "as-received") form, and following stabilization. The chemistry of plutonium dioxide and adsorption/readsorption of moisture on that oxide is complex and far from being fully defined. The plutonium processing sites (Hanford Site, or RL, the Rocky Flats Environmental Technology Site or RFETS, the Los Alamos National Laboratory, or LANL, and the Savannah River Site, or SRS) are committed, both to the Defense Nuclear Facility Safety board (DNFSB) as well as to other federal, state and local governments concerned with the safe storage of fissile material to specific time-lines with respect to packaging both metals and oxides according to DOE-STD-3013. In fact, "The Board continues to encourage DOE to place its hazardous material in a stable form and robust packaging in a timely manner as set forth in Recommendation 94-1".[4] The data contained in this paper was acquired as a result of attempting to support the DOE processing sites with the requirement to meet the moisture limit of 0.5 weight percent or less.

This paper describes some of the results obtained from exposing previously stabilized plutonium oxides to two very different atmospheres. The Los Alamos National Laboratory Plutonium Facility, TA-55, is the facility where the material is stabilized and a limited number of characterization tests are performed on both the as-received and the stabilized material. It maintains an atmosphere in the glove boxes of ~1% relative humidity. The second is the Chemistry and Metallurgy Research (CMR) facility also at the Los Alamos National Laboratory, with an atmosphere of 50-60% relative humidity. Varying results have been achieved by allowing the stabilized plutonium oxide to be exposed to the atmosphere of each facility.

EXPERIMENTAL PROCEDURES

Several items within the MIS program were selected to be reevaluated using moisture analysis techniques at the CMR building. Each item had been previously stabilized by calcination to 950^{o} C in a resistance heating furnace for two hours as required by the 3013 Standard. That calcination process involved evenly distributing the bulk oxide in a rectangular fused silica boat (18 cm * 28 cm * 8 cm deep) and then heating it in the furnace in an air atmosphere. This stabilization process is intended to accomplish the following objectives:

- Eliminate reactive materials such as finely devided metal or sub-stoichiometric plutonium oxides;
- Eliminate organic materials
- Reduce the water content to less than 0.5 wt.% and similarly reduce equivilent quantitites of species such as hydrates and hydroxides that might produce water;
- Minimize potential for water readsorption above the 0.5 wt% threshold; and
- Stabilize any other potential gas-producing constituents.[1]

Following the calcination, each item was blended in a v-blender for an hour to achieve the greatest homogeneity, then various samples were pulled from the material for characterization, such as particle size and surface area. Surface areas were determined with a Quantachrome Corporation Nova 1000 sorption analyzer using the BET (Braunauer-Emmett-Teller) method with N2 as the adsorbate**.** Particle size measurements were made with a Lasentech LAB-TECH NOVA 3000 analyzer, a laser system employing the light-scattering method for size measurements up to particle diameters of 250 micrometers.

The various items were then packaged and sent back down to the TA-55 vault for two to four years. In February of this year, many items were once again brought into the processing glove box of the main floor of TA-55.

Of the two main facilities which handle plutonium oxide at Los Alamos, the largest quantities of the material (called parent lots) are handled at TA-55. TA-55 was designed as a dry glove box environment to limit the oxidation of metal surfaces. Due to the need of TA-55 glove boxes to be used for kilogram quantity processing of plutonium, the majority of analytical techniques (requiring only milligram to gram quantities) are located at the CMR building. The primary moisture measurment techniques for analysis of radioactive materials at LANL are located at the CMR building. Samples are shipped between the two facilities on a regular basis. There are four moisture measurement techniques used at CMR which are currently being examined in this program: 1.) loss-on-ignition (LOI), 2.) super-critical fluid extraction (SFE), 3.) interstitial gas analysis (IGA), and 4.) thermogravimetric analysis (TGA). These moisture measurement techniques will not be evaluated in this paper. However, the results achieved with these techniques confirm the moisture uptake values which will be discussed here.

The plutonium oxide being evaluated in this experiment was obtained from a variety of chemical and metallurgical processes. It was received at TA-55 both from the Hanford Plutonium Processing Facilities as well as the Rocky Flats Environmental Technology Site (RFETS). One item was added to this group from the LANL TA-55 inventory because of its high uranium content (SCP711-56A). Adsorption data were obtained by repeatedly measuring the mass of an accurately weighed oxide sample sitting on an analytical balance. Doors of the balance chamber remained fully open except when measurements were being made. The samples exposed to the atmosphere at the CMR building were approximately 3 gram samples while the TA-55 samples were approximately 50 gram samples.

Table 1 Properties of Plutonium Oxide Used in Adsorption Experiments

Parent	**%Pu**	**Source Description**	**Maximum % Weight Change at 50% Relative Humidity**	**Maximum % Weight Change at 1% Relative Humidity**	**Time Since Stabilization**
X2165	34	Dissolution residuals	0.05	-0.04	2 yrs, 5 mos.
ARF295	37	Pyrochemical	3.6	-0.04	3 yrs, 10 mos.
O3038	57	Plutonium/uranium oxide	7.7	0.008	2 yrs, 8 mos.
J2201	65	Dissolution residuals	0.41	0.06	3 years
S1856	84	Peroxide precipitation/calcination	0.45	-0.12	2 yrs, 6 mos.
SCP711-56A	86	Carbide/nitride fuel oxidation	0.11	0.01	0

Moisture Uptake at TA-55

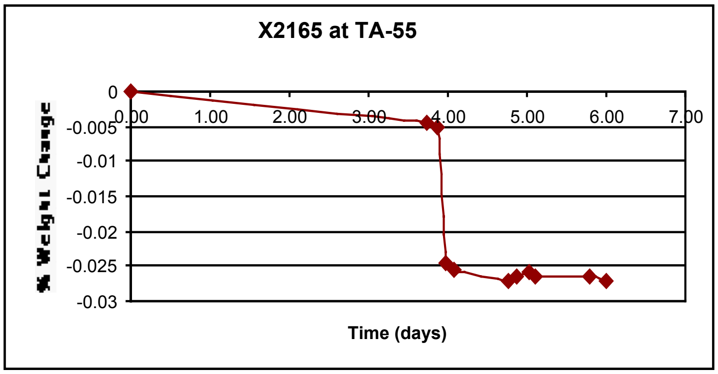


Figure 1a.

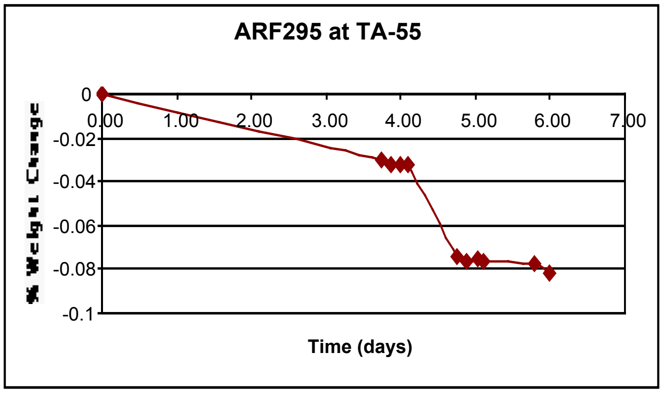


Figure 2a

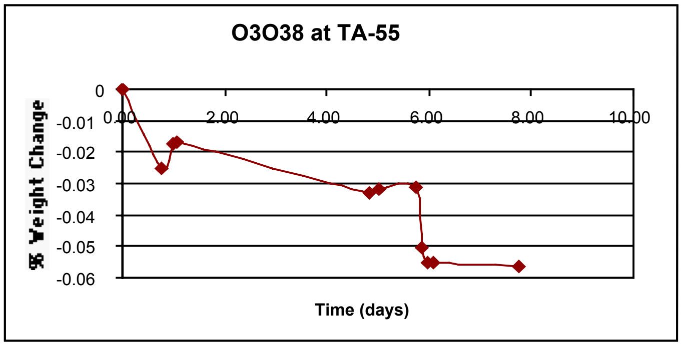


Figure 3a

Moisture Uptake at CMR

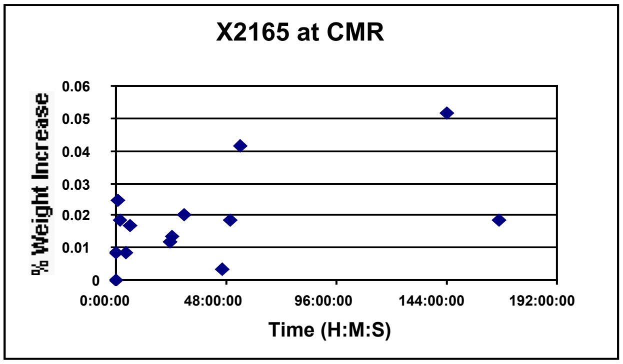
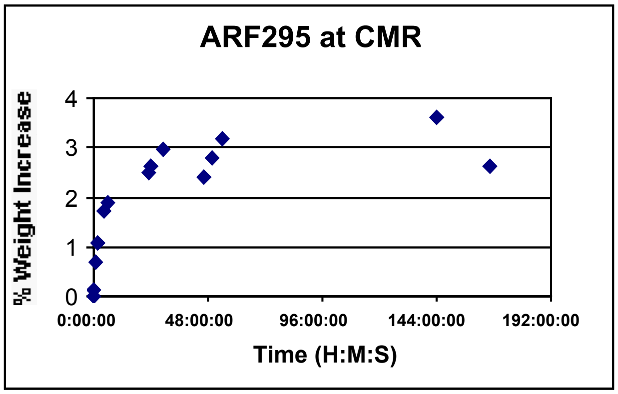


Figure 1b



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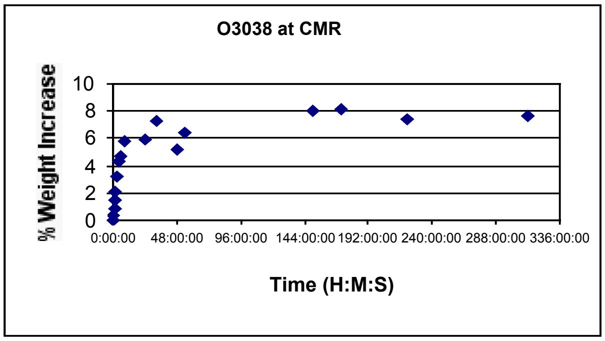

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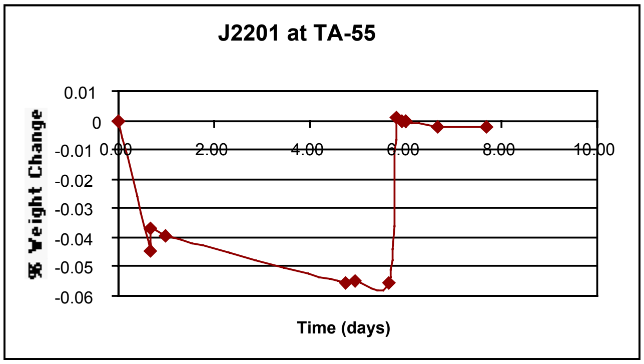

Figure 4a

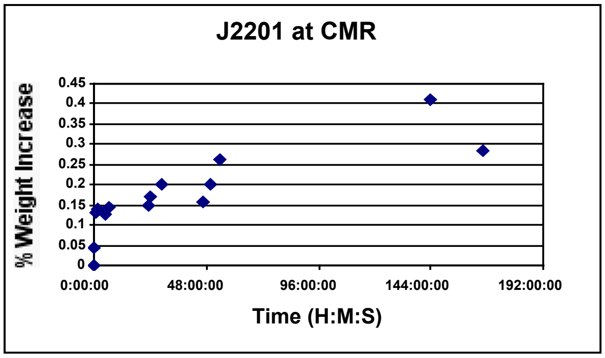

Figure 4b

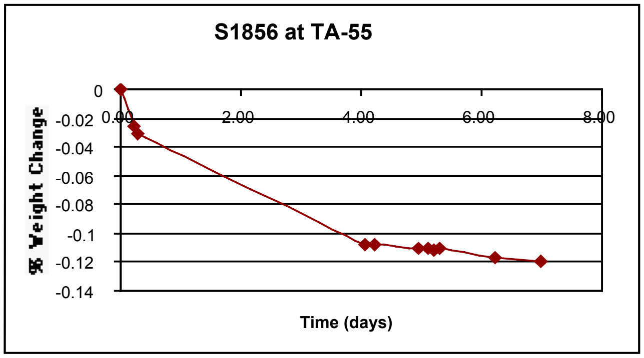

Figure 5a

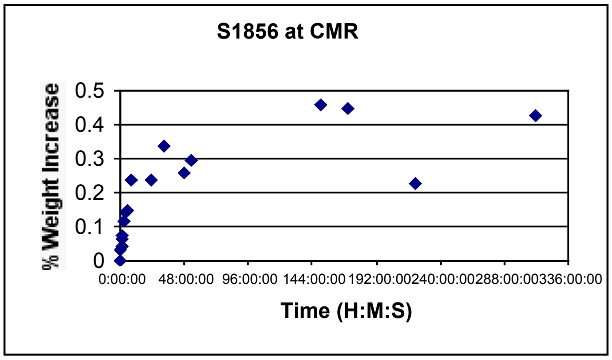

Figure 5b

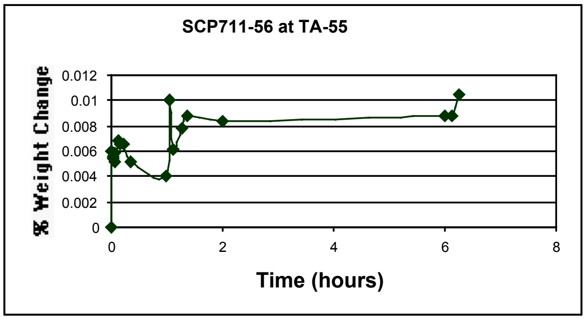

Figure 6a

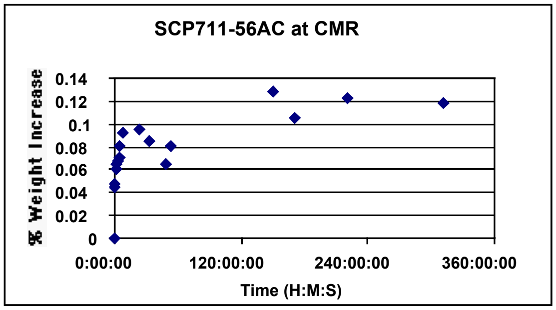

Figure 6b

DISCUSSION OF RESULTS

Each item shown above, with the exception of SCP711-56 showed a weight loss in the dry glove box at TA-55. The time dependence of moisture adsorption at the CMR building is indicated by a progressively decreasing rate until an equilibrium, or saturated condition is reached. This is in agreement with Hashke and Rickett's findings for >88 mass % plutonium.[3] The weight gain of SCP711-56 will be studied more closely by this program It is expected in mixtures of plutonium and uranium that at least two circumstances are occurring concurrently during stabilization: the conversion of UO_2 to U_30_8 (and therefore a weight gain) and adsorbates being driven off (a weight loss). The gain of moisture on plutonium oxide samples is not unexpected. Even the 3013 Standard warns: "Control of time and atmosphere between calcination and packaging is strongly advised when handling plutonium oxides containing magnesium and calcium chloride impurities to avoid the potential for concentrating unacceptable levels of moisture on other phases…"[1] What was not expected was the large difference between how the samples acted at TA-55, under extremely dry conditions, to the point of loosing weight after being reexposed to the glove box atmosphere and how they responded at CMR in a high humidity environment after being stabilized at 950 C. To behave so differently in the different environments confirms a statement by Hashke and Ricketts: "The surface of plutonium dioxide is chemically active and interacts strongly with adsorbates."[3] However, this moisture readsorption as a function of actinide content, particle size, or surface area is not clear or consistent.

Table 2 Characteristics of Plutonium Oxide Used in Adsorption Experiments

Parent	% Weight Change	Surface Area (m2/g)	Particle Size (µm)	Sum of Ca, K, Mg and Na Weight %
X2165	0.05	0.44	12.3	0.35
ARF295	3.6	Not available	6.8	8.82
O3038	7.7	0.21	10.4	6.53
J2201	0.41	18.94.	5.0	1.79
S1856	0.45	1.60	5.1	0.23
SCP711-56A	0.11	1.11	2.8	0.39

Table 2 shows % weight change, surface area, and particle size of the items considered in this paper. While O3038 has a high weight gain and low surface area, X2165 and S1856 also has a low surface area, but a low weight gain. J2201 has a very high surface area, but low weight gain. There is also not a direct correlation between large particle size and low surface, because particles of plutonium are not perfectly spherical, but contain crevices and cracks.

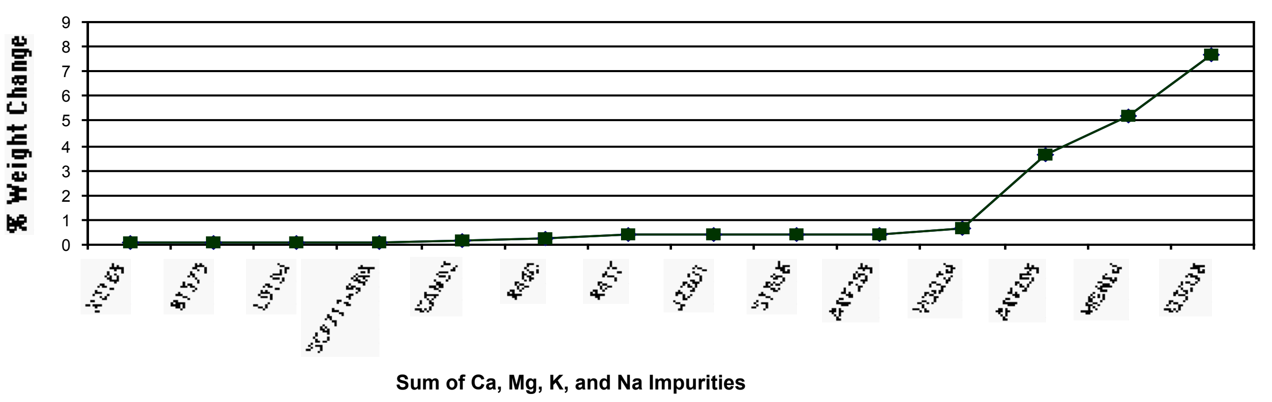

Figure 7 % Weight Gain as a Function of Salt Impurities

Figure 7 includes the values of weight gain and salt impurities for each of the items included in this paper. The additional eight moisture uptake graphs for the other parents were not included in this paper due to its length limitation. But a correlation between the variables is strong. More work is needed to confirm these results. If high salt-containing plutonium oxide is processed in a humid environment, readsorption of moisture should be expected, potentially enough to cause the material to fail the 3013 standard of 0.5 weight percent.

REFERENCES:

[1] DOE-STD-3013-99 “Stabilization, Packaging, and Storage of Plutonium-Bearing Materials”.

[2] “Criteria Defining a Material Represented in the MIS Inventory” (page 1).

[3] J.M. Haschke and T.E. Ricketts, “Adsorption of Water on Plutonium Dioxide”, Journal of Alloys and Compounds 252 (1997). 148-156.

[4] Letter from John Conway, DNFSB Chairman, to T.J. Glauthier, Deputy Secretary of Energy (December 6, 1999).

[5] J. M. Hashke and T.E. Ricketts, “Plutonium Dioxide Storage: Conditions for Preparation and Handling”.