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Evaluation of Plutonium Oxide Destructive Chemical Analyses for Validity of Original 3013 Container Binning

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ABSTRACT

The surveillance program for 3013 containers is based, in part, on the separation of containers into various bins related to potential container failure mechanisms. The containers are assigned to bins based on moisture content and pre-storage estimates of content chemistry. While moisture content is measured during the packaging of each container, chemistry estimates are made by using a combination of process knowledge, packaging data and prompt gamma analyses to establish the moisture and chloride/fluoride content of the materials. Packages with high moisture and chloride/fluoride contents receive more detailed surveillances than packages with

less chloride/fluoride and/or moisture. Moisture verification measurements and chemical analyses performed during the surveillance program provided an opportunity to validate the binning process. Validation results demonstrated that the binning effort was generally successful in placing the containers in the appropriate bin for surveillance and analysis.

INTRODUCTION

The termination of nuclear weapons production activities in the early 1990s left large quantities of surplus plutonium-bearing materials within the U.S. Department of Energy (DOE) complex. Some of the plutonium was in various stages of the manufacturing process, and the remainder was material in storage awaiting use or plutonium recovery. A DOE Technical Standard, DOE-STD-3013 (Ref. 1), was developed to specify the long-term requirements for storage of these materials for a period of time that could be as long as 50 years. The 3013 standard specifies stabilization, packaging and surveillance requirements to assure that these plutonium-bearing materials can be safely stored until final disposition. Because of the large number of containers that are to be stored, a statistically-based surveillance program was implemented to assure safety, while minimizing the risks and costs associated with storage and surveillance activities. The surveillance program included the "binning" of various 3013 packages according to the chemistry of the plutonium bearing materials stored in the package. The package chemistry used for binning process was based on the best available knowledge of the impurity composition. However, the surveillance activities included chemical analyses of the contents of selected packages and thus provided an opportunity to determine the validity of the package binning process. The validity determination is the subject of this paper.

BACKGROUND

THE PLUTONIUM-BEARING MATERIALS

At the beginning of the stabilization and packaging effort, there was a broad range of plutonium-bearing materials that required stabilization and packaging prior to long-term storage. These materials exhibited a wide range of chemical characteristics. At one compositional extreme was pure plutonium metal that was in the process of being manufactured into weapons components; at the other compositional extreme was a variety of impure scrap materials from processing and experimental programs that had been stored in vaults for decades awaiting plutonium recovery. In some cases, the only information available on the scrap material was the quantity of nuclear material present and the site of origin, which could be a DOE or commercial nuclear site involved in processing or research and development. In other cases, there are varying levels of "process knowledge" that describe how the material was generated and what possible impurities might be present. Chemical compositions of the material were very rarely available. However, the anticipated behavior of the package during storage depends on the chemistry of the plutonium bearing materials. The potential for corrosion depends on the presence of moisture, chloride salts and other materials variables as does the potential for pressure generation inside the sealed packages. Furthermore, the surveillance requirements for packages will vary with the potential for corrosion and/or pressurization. Therefore, process knowledge, site origin and other material information were used to evaluate the material chemistry and bin the various packages according to the estimated potential for corrosion and/or pressurization during long-term storage.

THE STANDARD

The 3013 Standard took a one-size-fits-all approach. The Standard specifies robust stabilization and packaging requirements that, based on the best available knowledge, are adequate for the highest risk material to be safely packaged and stored. This approach resulted in very robust stabilization and packaging requirements while eliminating the huge costs associated with analyzing and characterizing the chemistry of each of the thousands of containers of material prior to packaging. There was no experience storing such a wide variety of plutonium-bearing materials for up to 50 years in welded containers, so to bridge this experience gap, the 3013 Standard requires a surveillance program for the stored 3013 containers. The Standard encourages the use of a statistical selection approach so that a high level of confidence can be obtained while minimizing the risks and costs associated with surveillance activities. The statistical approach being used by the surveillance program is discussed in detail in Ref. 2.

BINNING BY FAILURE MODE

The 3013 containers are welded, corrosion resistant stainless steel vessels. The outer container is a qualified pressure vessel with a design pressure of 4920 kPa (699 psig) (Ref. 1). Only two credible failure mechanisms have been identified for these containers: corrosion or over-pressurization. To set up an effective statistically based surveillance program, the inventory of 3013 containers was split into three population groups or bins. The first bin is the Innocuous Bin (I) which includes items that are believed to present a minimum likelihood of container failure. The "I" Bin containers are those whose contents are plutonium metal and high purity plutonium oxide with minimum adsorbed moisture. The second bin is the Pressure Bin (P), which include containers that have the potential for gas generation with associated container pressurization. The "P" Bin containers are those whose contents are impure oxides with no chloride or fluoride content, as well as pure oxide containers whose moisture content are above a specified low threshold (but still below the maximum 0.5 wt% specified by the 3013 Standard). The third bin is the Pressure and Corrosion Bin (P&C), which includes containers believed to have the potential for both corrosion of the stainless steel container as well as gas generation and the associated container pressurization. The "P&C" Bin containers are those whose contents include chloride- and/or fluoride-contaminated plutonium oxides.

The data necessary to assign the containers to the appropriate bins are: plutonium oxide purity, moisture content, chloride content, and fluoride content. Actinide content is measured for each of the containers to establish the amount of special nuclear materials (in this case U, Np, Pu, and Am) in each container. Since the mass of the oxide is known, the purity of the plutonium (wt% Pu) can be calculated for each container. The 3013 Standard requires that measurements be made to assure that the moisture content of each 3013 container is below 0.5 wt%. Because of the uncertainties associated with measuring moisture content, a conservative moisture content is assigned to each container. Since the content of each 3013 container was not sampled and analyzed for chloride and fluoride content, Prompt Gamma (PG) (Ref. 3) analyses were performed on the impure oxide containers after packaging. This nondestructive technique can be utilized to detect chloride and fluoride content in the 3013 containers; however, the minimum detection limit for chloride (approximately 8000 ppm) is above the concentration that could potentially cause corrosion. The method is more sensitive for fluoride determination as the PG detection limit for fluoride (approximately 900 ppm). For these reasons, PG is used in combination with process knowledge to identify whether chloride and/or fluoride may be present in the container. The most recent binning results are documented in Ref. 4.

The surveillance approaches for the three bins are different. Pressurization can be detected during non-destructive examination (NDE) by radiographing the inner container and measuring lid deflection. Internal corrosion can only be detected by performing destructive examination (DE). For this reason, NDE is appropriate for I and P Bin containers while DE is necessary for characterization of items from the P&C Bin. DE was also performed on a sampling of containers from the P Bin as a method to baseline the NDE process.

A conservative approach was taken during the binning process (Reference 2). Since the most extensive examination is performed on containers in the P&C Bin, if either process history information or PG analysis indicated that chloride or high fluoride content may be present, the container was placed in the P&C Bin. Likewise, only containers with the purest oxide and lowest moisture content were placed in the I Bin. The binning of containers is routinely re-evaluated as additional containers are generated and based on results from surveillances that may affect the binning of specific containers.

DESTRUCTIVE EXAMINATION

A portion of the destructive examination program involves sampling the contents of the 3013 packages to characterize the chemical composition of the stored materials. Specific protocols were developed for sampling and analysis of the can contents.

SAMPLING

The 3013 packages were opened in a glovebox at the SRS K Area Material Storage Facility. An initial solid sample was taken immediately after opening each convenience can (the inner-most container in the 3013 package). This sample, referred to as the initial moisture (IM) sample, was immediately placed in an air-tight stainless steel ampoule (B-vial) and was subsequently analyzed by thermogravimetric analysis -mass spectrometry (TGA-MS) to determine the moisture content of the material (which is assumed to be representative of the condition of the solid when it was in the 3013 package). This analysis produces two results, the total mass loss from TGA as the sample is heated from ambient temperature to 1000 °C, and the fraction of the mass loss that is due to moisture as determined from the MS data. These results can subsequently be compared to the baseline result reported by the packaging site.

The remaining solid was then removed from the convenience can and poured into a rectangular tray and spread out to cover the entire surface of the tray; an aliquot was taken from each of four quadrants of the tray, and the four aliquots were combined to make a single sample. It was from this sample that a sub-sample (hereafter referenced as the representative or "RP" sample) was selected. The RP sample is loaded into a uniquely-numbered B-vial and transferred to Savannah River National Laboratory (SRNL) for analysis. While the material was in the tray, it was visually inspected. If there were items present in the tray that were unique, such as piece of oddly colored or shaped material, some portion of the unique material, referred to as the if required "IR" sample, was collected and loaded into a uniquely numbered B-vial and sent to SRNL for analysis.

MOISTURE MEASUREMENT

A 3 gram (nominally) sample is removed from the sealed ampoule, placed in a high-fired alumina crucible, and introduced to the TGA-MS. After purging the sample furnace with high purity Ar gas (a carrier gas), for approximately 10 minutes, the crucible and sample are heated from room temperature to 1000° C at a rate of 15 ° C per minute. The mass loss is continuously measured as a function of time and temperature. The gas generated is sent through the MS and m/z 17 and 18 signals are measured as a function of temperature. These results, along with calibration data collected on samples of known moisture content, allow the use of the MS data to quantify the amount of water lost by the sample, which is assumed to be the moisture content of the sample.

CHLORIDE AND FLUORIDE CONTENT MEASUREMENT

The PG analyses of the packaged materials provide an estimate for the fluoride and chloride contents of the solids in the package. To characterize the water-soluble chloride and fluoride content of the solids, aqueous leaching at 90 °C for 3-hours was utilized to solublize the water-soluble fraction of the sample. Two aliquots of 1-gram each of the RP sample were leached in de-ionized water. Each sample to be leached was transferred to a flat-bottomed, screw lid 60-mL polypropylene reaction tube. Each tube was placed in a thermostated hot block heater capable of containing six reaction tubes. During each run, the hot block contained the two reaction tubes, a blank, and a "dummy" tube containing water into which a thermocouple was inserted (for an independent temperature measurement to which the thermostated hot block controller could be compared). A small watch glass (filled with water to condense the water vapor evaporating from the solution) was placed over the lid of the tube, and the temperature was ramped up to ~90 °C over a period of 60 to 90 minutes. After temperature stabilization, the temperature was held constant for 3 hours. After the hot block had returned to ambient temperature, the volume of each leaching tube was checked and the solution volumes were adjusted, as necessary, to 30 mL using deionized water. The solid-solution mixtures were filtered through a 0.45 µm filter in 10 mL increments, and the resulting solutions were subjected to Ion Chromatography (IC) and Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) analyses to determine the concentrations of the aqueous species of interest. Since most chloride salts have a high solubility in water, this technique is expected to accurately measure the total chloride content in the sample. But since many fluoride compounds have low solubility in water, these results are expected to under-report the total fluoride content of the sample.

RESULTS AND DISCUSSION

DESTRUCTIVE EXAMINATIONS

Moisture Content

Moisture content is analyzed by TGA-MS. Table 1 shows the moisture results reported by the packaging site and the moisture results from SRNL DE measurements (IM samples). The packaging sites utilized one of four experimental methods to determine moisture contents of the packages material: loss-on-ignition (LOI); TGA; Fourier Transform-Infrared Spectroscopy (FTIR) in tandem with TGA (TGA-FTIR); and TGA-MS. The goal of the packaging site moisture analysis was to assure that 0.5 wt% was not exceeded and as such, some of the recorded values are over-estimates of the actual moisture content. Loss-on ignition (LOI) and TGA can significantly over-report water content since these techniques report all mass loss as water, while neglecting the fact that some of the chloride salts present in these materials have considerable vapor pressures at 1000 °C. Since TGA-FTIR and TGA-MS measure the amount of water driven off of the sample, results using these techniques most accurately reflect the true moisture content of the sample. The SRNL DE analyses utilized TGA-MS to measure the moisture content of the surveillance samples. As shown in Table 1 the packaging site-measured moisture content of each package surveilled falls below 0.5% by mass. As expected, the SRNL moisture values are either the same (within measurement uncertainties) or lower than the values reported by the packaging sites.

Chloride and Fluoride Content

Table 1 summarizes the chloride and fluoride results from SRNL IC analyses. DE results from 43 containers were available for this review. For 40 of the containers, the chloride results are consistent with the baseline PG estimates. For two containers, significant levels of chloride (58000 ppm and 20000 ppm) were reported in the baseline PGs but chloride was not detected in either the surveillance PGs or the chemical analyses. For one container, no chloride was reported in the baseline PG, but chloride was detected in both the surveillance PG (34000 ppm) and chemical analyses (37500 ppm).

Because of the low solubility of fluorides in water, the fluoride results in general are significantly below those indicated by PG. There were no cases where significant fluoride was found in any P Bin containers.

SUMMARY AND CONCLUSIONS

The DOE Technical Standard, DOE-STD-3013 (Ref. 1) was developed to specify stabilization, packaging and surveillance requirements to assure that the excess plutonium can be safely stored until final disposition. The standard was written to address storage for a period of time which was assumed to be up to 50 years; however, there was insufficient historical experience available to predict the behavior of these materials in hermetically sealed packages for such a long time interval, so a surveillance program was developed to investigate the behavior of the stored materials, and the material-package interactions. Because of the large number of containers that are to be stored, a statistically-based surveillance program was implemented to assure safety, while minimizing the risks and costs associated with surveillance activities. The data collected during destructive surveillance activities have been compared to the known process history for the oxide in the containers and non-destructive measurements performed on the containers.

DE results for 43 containers were available for this review. For 40 of the containers, the results show that the binning effort successfully assigned the correct surveillance bin. There were three containers that were not assigned to the correct bin. Two containers had been assigned to the P&C Bin, but DE results show that corrosive impurities were not present. One container was assigned to the P Bin, but DE results show the presence of a significant concentration of chloride impurities. In all three of these cases, the PG performed during surveillance showed chloride and fluoride concentrations that were consistent with the DE sample results. It appears that there was an error in the reported baseline PG for these three containers. The results indicate that if the baseline PG is correct, the containers will be binned appropriately, however, there is the potential for the data packages to include incorrect baseline PGs.

The binning of containers is routinely reassessed and the results from surveillance activities are incorporated in the reassessments. For example, since these surveillances show that the three containers were in the incorrect bin, the containers are no longer valid containers for their former bin samples. As a result, the next re-binning will select additional, replacement containers for the bins. In addition, during the next re-binning, all baseline PGs will be reevaluated for possible errors.

DE of selected P&C Bin containers is currently scheduled to continue through FY2017. The results from the surveillances will be used to establish future surveillance requirements for containers in the P&C Bin. The surveillances of the initial sampling of P Bin and I Bin containers was completed in 2009. Those results are being evaluated to determine what level of surveillance will be needed for those bins in the future to evaluate longer term aging effects in containers that are basically free of chlorides. The results of these determinations will also be applied to new, chloride/fluoride free, P Bin and I Bin containers that are generated during future packaging operations.

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Table 1. Characteristics of DE Samples

Sample	Actinide Content/ (wt%)	Bin	Baseline Moisture (wt%)	Baseline Moisture Method	DE TGA Mass Loss (wt%)	DE TGA-MS Moisture (wt%)	Cl Concentration (ppm)			F Concentration (ppm)		
							Baseline PG	Surveillance PG	Surveillance IC*	Baseline PG	Surveillance PG	Surveillance IC*
R600885	86.4	P	0.11	LOI	0.04	0.05	ND	ND	118	ND	ND	555
R601722	84.3	P	0.18	LOI	0.16	0.04	ND	ND	355	2800	2700	498
R601318	83.6	P	0.17	LOI	0.08	0.02	ND	ND	<465	7100	6700	<465
H002088	86.7	P	0.22	TGA	0.23	0.23	ND	ND	150	ND	ND	<150
H003119	70.8	P	0.18	TGA	0.41	0.09	ND	34000	37500	5100	1300	230
H001916	34.3	P	0.06	TGA	0.06	0.06	ND	ND	301	3800	3200	<175
R601957	87.5	P&C	0.03	LOI	0.03	0.04	ND	ND	<500	ND	ND	<500
R600719	86.2	P&C	0.10	LOI	0.03	0.04	ND	ND	<500	ND	ND	<500
R610735	53.4	P&C	0.24	FTIR	4.10	0.19	85000	84000	168000	ND	500	166
R610697	69.8	P&C	0.12	FTIR	0.44	0.06	91000	85000	105000	ND	ND	<600
R601285	85.8	P&C	0.15	LOI	0.06	0.10	5000	ND	316	ND	ND	<600
R602731	97.4	P&C	0.07	LOI	0.10	0.03	ND	ND	<438	ND	ND	<438
H000898	77.7	P&C	0.14	TGA	0.19	0.04	ND	ND	<451	10000	4200	393
R610327	80.8	P&C	0.39	TGA	1.31	0.04	No Data	ND	518	No Data	ND	339
R610298	64.8	P&C	0.16	TGA	0.20	0.14	91000	82000	98000	ND	300	<303
R610324	71.6	P&C	0.07	TGA	0.17	0.10	100000	80000	76000	ND	ND	<300
H001992	52.3	P&C	0.37	TGA	0.27	0.05	ND	ND	322	17000	23000	3650
H003157	85.0	P&C	0.19	TGA	0.21	0.10	ND	ND	<161	10900	ND	<161
R610584	71.4	P&C	0.15	FTIR	1.05	0.07	ND	ND	1860	7600	7400	361
R610578	64.7	P&C	0.04	TGA	0.19	0.19	53000	50000	41000	12000	10000	<157
H003409	74.0	P&C	0.29	TGA	0.49	0.29	68000	62000	52000	ND	800	<150
H002573	74.3	P&C	0.37	TGA	0.56	0.33	74000	57000	67000	ND	ND	<157
H002534	70.5	P&C	0.35	TGA	0.55	0.19	73000	63000	64000	ND	ND	<152
R610679	70.4	P&C	0.26	TGA	0.30	0.03	ND	ND	<151	8200	7600	300
H002750	69.6	P&C	0.07	TGA	0.16	0.07	3800	ND	1720	1600	1300	814
H004099	78.9	P&C	0.23	TGA	0.09	0.03	58000	ND	<157	ND	2800	<157
H004111	71.8	P&C	0.40	TGA	0.55	0.26	85000	63000	58100	ND	ND	<150
H002554	70.6	P&C	0.32	TGA	0.37	0.22	81000	60000	65600	ND	ND	<151
H001941	60.1	P&C	0.06	TGA	0.17	0.02	ND	ND	516	6000	6600	6220
R602498	81.6	P&C	0.26	LOI	0.17	0.13	20000	12000	7450	ND	ND	150
H002509	70.7	P&C	0.39	TGA	0.65	0.26	62000	64000	58400	ND	ND	<151
H002565	70.1	P&C	0.39	TGA	0.38	0.25	93000	69000	75500	ND	800	<150
H002657	77.4	P&C	0.23	TGA	0.28	0.22	13000	33000	29400	ND	ND	<150
R611398	70.8	P&C	0.29	FTIR	0.02	0.02	ND	ND	151	4700	5000	151
H002200	71.1	P&C	0.22	TGA	0.33	0.03	ND	ND	151	21000	20000	1060
H002667	72.4	P&C	0.23	TGA	0.46	0.19	90000	64000	72500	ND	ND	<150
H002715	70.3	P&C	0.38	TGA	0.68	0.28	87000	68000	77600	ND	ND	<151
R610700	65.4	P&C	0.23	TGA	0.37	0.03	ND	ND	<150	10000	8800	160
R610764	62.6	P&C	0.06	TGA	0.28	0.05	61000	54000	74000	ND	ND	<618
R610573	63.5	P&C	0.25	TGA	0.63	0.22	46000	50000	34200	3400	28000	150
R610558	87.9	P&C	0.04	TGA	0.05	0.01	ND	ND	<151	9600	8600	<151
R610806	76.7	P&C	0.28	TGA	0.75	0.27	39000	30000	20300	9300	7500	<151
H002195	84.2	P&C	0.11	TGA	0.15	0.01	20000	ND	<151	ND	ND	<151

* IC results are from ion chromatography of aqueous leach solution from the sample. Only water soluble species are detected.