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Material Properties of Plutonium-Bearing Oxides Stored in Stainless Steel Containers

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Abstract

The destructive examination (DE) of 3013 containers after storage is part of the Surveillance and Monitoring Program based on the Department of Energy's standard for long-term storage of Pu (DOE-STD-3013). The stored, Pu-bearing materials may contain alkali halide contamination that varies from trace amounts of salt to about 50 weight percent, with smaller fractions of other compounds and oxides. These materials were characterized prior to packaging, and surveillance characterizations are conducted to determine the behavior of the materials during long term storage.

The surveillance characterization results are generally in agreement with the pre-surveillance data. The predominant phases identified by X-ray diffraction are in agreement with the expected phase assemblages of the as-received materials. The measured densities are in reasonable agreement with the expected densities of materials containing the fraction of salts and actinide oxide specified by the pre-surveillance data. The radiochemical results are generally in good agreement with the pre-surveillance data for mixtures containing "weapons grade" Pu (nominally 94% ^{239}Pu and 6% ^{240}Pu); however, the ICP-MS results from the present investigation generally produce lower concentrations of Pu than the pre-surveillance analyses. For mixtures containing "fuel grade" Pu (nominally 81-93% ^{239}Pu and 7-19% ^{240}Pu), the ICP-MS results from the present investigation appear to be in better agreement with the pre-surveillance data than the radiochemistry results.

Introduction

The destructive examination (DE) of the Pu-bearing materials from 3013 containers is part of the Surveillance and Monitoring Program based on the Department of Energy's requirements for long-term storage of Pu (DOE-STD-3013).¹ The materials studied in this investigation include plutonium oxide materials only; no metallic items were investigated. Nevertheless, these oxide-based materials exhibited a wide range of chemical characteristics. At one compositional extreme was nearly pure plutonium oxide. At the other compositional extreme is a variety of impure materials from processing and experimental programs that had been stored in vaults for decades awaiting Pu recovery. In some cases, the only information available on the scrap material was the quantity of nuclear material present and the site of origin. In other cases, there are varying levels of "process knowledge" that describe how the material was generated and what possible impurities might be present. Alkali metal-halide salts, which are a result of the molten salt² processing associated with weapons production, are the primary contaminant in these materials. This halide salt contamination varies from trace quantities to about 50 weight percent. Other non-actinide metals, halide salts, and compounds may also be present, but generally at much lower concentrations than the alkali metal-halide salt contamination.

The materials being investigated have been in storage in 3013 containers for 4 to 7 years. A variety of characterization techniques have been utilized to deduce the chemical and phase composition of these materials. The characterization techniques include:

density determination,

dissolution/leaching studies,
inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-emission spectroscopy (ICP-ES), and radiochemical analyses of dissolution products,
ion chromatography (IC) and ICP-ES analyses of aqueous leachates,
moisture content determination,
surface area determination, and
phase and elemental characterization by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), respectively.

Samples of contents from twenty-eight 3013 containers that originated at the Hanford or Rocky Flats sites are included in this investigation. All handling of the initial samples, including removal of material from the 3013 containers, was performed in gloveboxes under air atmosphere. This paper describes the material characterization methodologies, presents the results of the characterizations and compares the results with pre-storage characterization results.

Experimental

SAMPLING

The 3013 containers were opened in a once through air glovebox at the Savannah River Site's K Area Material Storage Facility. An initial sample of the Pu-bearing material was taken immediately after opening each convenience can (the inner-most container in the 3013 container). This sample, referred to as the initial moisture (IM) sample was placed

in an air-tight stainless steel ampoule (B-vial) and was analyzed by TGA-MS to determine the moisture content of the material (which is assumed to be a representation of the condition of the solid just prior to opening the 3013 container).

The solid was then poured from the convenience can into a rectangular tray and spread out to cover the entire surface of the tray. (Figure 1) A sample was taken from each of four quadrants of the tray and the four samples were combined to make a single sample for analysis. It was from this sample that a sub-sample (hereafter referenced as the representative (RP) sample) was selected, 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. Unique items, such as pieces of oddly colored or shaped material referred to as ‘if required’ (IR) samples, were collected and loaded into a uniquely numbered B-vial and sent to SRNL for analysis. The decision to take such a sample is based solely on engineering judgment. The surveillance engineer looks for foreign material that is different in appearance than the bulk of the oxide. (Figure 2) If such material is present an IR sample is taken. In addition to the IM, RP and IR samples, final moisture (FM) sample was collected just prior to repackaging the solids, and sent to SRNL for determination of the moisture content of the repackaged material.

CHARACTERIZATION OF AS-RECEIVED SAMPLES

Density Determination, Visual Inspection, and Sub-sampling

The density of each RP sample was determined by He gas pycnometry (Micromeritics AccuPyc model 1330 He Gas Pycnometer); the bulk density of each sample was

measured using a calibrated graduated cylinder. Generally 50% or more of the sample was subjected to density determination by pycnometry while the entire sample was used for the bulk density determination. The bulk determination was performed first. The RP sample was transferred into a weighed and calibrated 10-mL graduated cylinder resting on a flat, level surface, and the volume of the material in the cylinder was recorded. The graduated cylinder was weighed and the mass of the RP solid in the cylinder was determined. The average level of solid in the cylinder was computed from the high and low level measurements and these measurements were used to compute the average volume of material. The bulk density was computed by dividing the mass of the solid by the average volume. Upon completion of the bulk density determination, the pycnometry density determination was performed. The pycnometer determines the volume and density of the material three times, and then computes the average volume and density.

Upon successful completion of the density determination, the material was poured into a clean glass Petri dish, visually inspected, and photographed. If the particle size distribution of the material did not appear to be uniform, the material was ground with an alumina mortar and pestle, and the pycnometry and bulk and tapped density measurements were repeated. Upon completion of the inspection and size reduction (when required), the material was sub-sampled for additional analyses. Portions of the solid were taken for dissolution, aqueous leaching, surface area determination, SEM/EDS, and XRD.

Dissolutions

The dissolution studies were performed to produce aqueous solutions for characterization of the elemental content of the material. Because the chemical compositions, phase compositions, and solubilities of the materials were not known, two dissolution regimens were utilized. Both were based on the use of nitric acid-hydrofluoric acid media, but one of the dissolutions also included the addition of a complexant, boric acid, to the dissolver solution in an attempt to complex halides present in the solution (which would, in turn, reduce the likelihood of PuF_4 precipitation).

Two aliquots of 0.25-grams each were removed from each sample lot for dissolution studies. Each sample to be dissolved 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 holding 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 (as an independent temperature measurement to which the thermostated hot block controller could be compared). During some runs a second dummy tube (containing silica sand) into which a second thermocouple was inserted was also used (in an attempt to determine the temperature of the material in the reaction tubes).

To each sample-containing tube and each blank tube, a 30-mL aliquot of 12 M HNO_3 -0.2 M HF (nominal concentration) was added. A small polypropylene “watch glass” was placed over the lid of each tube, and the temperature was ramped up to $\sim 95^\circ\text{C}$ over a period of 60 to 90 minutes; each watch glass was filled with water to facilitate

condensation of vapor emanating from the solution. After temperature stabilization, the temperature was held constant for 3 hours. Just prior to de-energizing the hot-block, 2.5 mL of 0.9 M H_3BO_3 was added to the complexed dissolution tube, and then the temperature of the hot block was allowed to cool to ambient temperature. After the tubes had returned to ambient temperature, the volume of each dissolution tube was checked and the solution volumes were adjusted, as necessary, to 30 mL using deionized water. For samples believed to be high in chloride, a condenser containing permanganate-coated media was utilized to capture acidic vapors.

The solid-solution mixtures were filtered through a 0.45- μm acid-resistant filter in 10 mL increments. The resulting solids were dried to a constant mass at 120 °C, in a Mettler-Toledo model HR83 Moisture Analyzer. A portion of the recovered solids were subjected to XRD analysis. The resulting filtered solutions were subjected to ICP-ES, ICP-MS, and radiochemical (α and γ spectrometry) analyses to determine the cation concentrations in the solutions.

In addition to two dissolution samples, two aliquots of 1-gram each were leached in 30 mL of de-ionized water. A small watch glass was placed over the lid of the tube, and the temperature was ramped up to ~90 °C, generally over a period of 60 to 90 minutes. A lower temperature was utilized, as compared to the dissolutions, to retard the evaporation of chlorine-containing vapor species. 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 resulting solutions were subjected to IC and ICP-ES analyses to determine the concentrations of the cations and anions of interest.

Results and Discussion

In an attempt to determine the chemical composition of the initial solids, the resulting solution and any recoverable insoluble solids were analyzed. The results of the analyses performed to characterize the initial solids are presented in the attached tables; however, it is outside the scope of this discussion to discuss all of the analytical results related to the interrogation of these samples, so only those results germane to the discussion of the characterization of the chemical and phase compositions will be presented and discussed.

AS-RECEIVED SAMPLES

Characterization of the as-received samples by XRD (see Table 1) suggests that these materials are, as expected, PuO₂ (and sometimes uranium oxide phases as well) accompanied by a variety of contaminants. Based on the pre-surveillance data reports, the 3013 materials can be conveniently classified as high purity oxide materials, containing ≥ 75 weight percent (%) Pu, and low-purity materials containing less Pu. In general, all of the samples contain varying quantities of simple oxide phases such as NiCr₂O₄, NiO, SiO₂, and Cr₂O₃. Some of the samples also contain other more complex oxide phases such as aluminosilicate and tungstate phases.

The presence of the Ni, Cr, Fe, aluminosilicates, and silica is not surprising. During the calcination process prior to 3013 loading, all of these materials were heated in air at 750 or 950 °C. Generally, the material was contained in an Inconel[™] or Hastelloy[®] tray during the calcination process. While these alloys are designed to be corrosion resistant,

some corrosion, in the form of surface oxidation, is common.³ The thin oxide coating can spall from the tray and contaminate the Pu-bearing material, and is often found as thin flakes of bluish-hued material. The silicon-containing phases found in these materials, such as silica and aluminosilicates, are probably contaminants that spall from the furnace lining (the refractory furnace lining is often fabricated from mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$, and/or a silica-containing composite material).

A portion of each as-received sample was subjected to SEM and XRD analyses.

Generally the XRD results show that the low-purity samples contain halide salts while the results from high-purity samples show no reflections that appear to result from halide-containing phases; the only exception to this behavior is H001992, for which the XRD results show numerous oxide phases, but no halide phases. While the phase characteristics of these samples are interesting, these results are qualitative in nature, and do not necessarily shed light on the quantitative chemical composition of the materials.

SEM analyses were performed to provide a preliminary elemental analysis of these materials. Energy dispersive spectra were collected on samples selected during visual inspection of the material. The spectrometry results for each sample were compared to pre-surveillance data to corroborate the most abundant metal present in the materials. These data were particularly useful for items that contained both U and Pu, since the SEM results could verify the presence of both actinides.

‘IF REQUIRED’ SAMPLES

‘If required’ samples were taken on a few occasions. In some of these cases, the IR sample contained elements and phases that suggest they were spalled oxide from the Inconel™ or Hastelloy® tray used in the calcination process. In the remainder of the cases, the IR sample appeared to be spalled refractory insulation from the calcination furnace. These conclusions are based primarily on the SEM analysis.

DENSITY MEASUREMENTS

As previously stated, both bulk and pycnometry density measurements were performed and values are shown below (Table 2). In an attempt to evaluate the reasonability of the pycnometer data, these results were plotted versus the actinide fraction for each sample, as taken from the Pre-Surveillance Data Report (a compendium of information on each item which includes the results of any analyses performed on the material before, during, or after packaging). The line on Figure 3, extending from 2.2 g/mL (the approximate density of KCl and NaCl) to 11.46 g/mL (the theoretical density of pure PuO₂), is included as an evaluation tool. As shown on the plot, most of the values fall close to the line, as would be expected if it is assumed the density of a mixture of PuO₂ and the chloride salts is a linear combination of the phases involved. There is one clearly discordant point at (97.43 wt%, 9.42 g/mL). The uncertainty in the actinide content of this sample, R602731 ([U]=41.48%, from ICP-MS results), could be as great as 30% because the pre-surveillance actinide content was computed from a γ assay of the

material and this sample is high in uranium (^{235}U has a weak γ , thus the high uncertainty in the assay).

DISSOLUTIONS

To perform elemental analyses on solids, it is generally necessary to digest the solids to produce a liquid sample. The common practice when dissolving materials containing refractory oxides, especially materials that contain high-fired PuO_2 , is to use a highly concentrated strong acid, such as HNO_3 to digest the material, accompanied by a complexant, such as F^- , to stabilize the aqueous Pu species in solution and drive the dissolution reaction to completion (per Le Chatelier's principle).⁴ When F^- is used as the Pu complexant, this approach sometimes leads to dissolution of the oxide followed by precipitation of PuF_4 . In an attempt to combat "post-dissolution precipitation", a second complexant is added after the initial dissolution process is completed to compete for the anionic complexant (in this case F^-).

During the present study, we utilized two dissolution flowsheets for each sample. Both employed 12 M HNO_3 -0.2 M HF for sample digestion; however, boric acid was added to the dissolver product of one dissolution (hereafter referred to as the complexed dissolution) before allowing the solution to cool. The residues recovered from the dissolution testing indicate that the complexed dissolution provides a more thorough mechanism for solubilizing the samples of interest (as shown in Table 3); consequently, most of the discussion of the experimental results shall address the results from the complexed dissolutions.

Twenty-eight samples were subjected to the complexed dissolution method; of those, only nine showed Pu-bearing phases in the insoluble solids. In seven of those cases with recovered solids, the only Pu-bearing phase was a fluoride, suggesting the dissolution process had successfully digested the PuO₂ (all of the starting materials showed Pu present as PuO₂), but that Pu-bearing phases subsequently precipitated from the solution due to the high ionic strength and [F⁻] of the solution. In only two cases, H002573 and H002554, did the Pu-bearing phase(s) in the insoluble solids include PuO₂, and in both of those cases, the insoluble solids accounted for less than 10% of the initial sample mass. Based on these results, it is concluded that the solutions produced by the complexed dissolution scheme give a reasonable representation of the chemical composition of the solid samples.

Another result of interest is related to the graphite present in H000898 (Table 1) and R610584 (Table 3). It is believed that the graphite in these samples is a result of material processing performed prior to these materials being selected for 3013 storage. Graphite is often used as a mold material during the casting of Pu, so it is likely that the graphite in these two materials was a result of mold material that accompanied the material through the casting and oxidation processes. If the pieces of graphite were large enough, it is possible that they were not completely oxidized during the numerous heat treatments to which these materials were subjected; consequently, they were transferred to the 3013 container along with the Pu-bearing materials.

CHEMICAL ANALYSES

The aqueous leach solutions were analyzed by IC (Table 4) and ICP-ES (Table 5).

The dissolution samples were analyzed by ICP-ES, ICP-MS, and radiochemical methods, α and γ spectroscopy; the results of these analyses are shown in the Table 6 and Table 7. In addition to the previously-mentioned analyses, the early aqueous leach solutions were also analyzed to detect any leaching of Pu- and/or U-bearing solids. The results of the analyses of these solutions confirmed the concentrations of Pu and U were at background levels, so these analyses were discontinued and will not be discussed further.

ICP-ES Analysis of Dissolution and Aqueous Leach Solutions

The ICP-ES results were used to identify the major, non-radioactive cations present in the dissolved solids. The major metallic contaminants generally included the alkali metals Na and K, the alkaline earth metals Ca and Mg, and the d-transition elements Ni, Fe, and Cr. In addition, one of the samples, R610327 contained 1 wt% Be, while two others (R610584 and R610578) each contained more than 0.1 wt% Be. All other cations detected were generally below 0.1 wt% (1000 ppm). It was recognized that the high ionic strength of the acidic solutions might impede the dissolution of water-soluble ionic compounds, such as KCl and NaCl, so aliquots of each solid were also subjected to aqueous leaching and the resulting solutions were also subjected to cationic analysis by ICP-ES.

For elements that are expected to be present as oxides, such as Fe, Cr, and Ni, the acid dissolutions resulted in solutions with higher concentrations than those from the aqueous leaches. For elements expected to be present as halides, Na and K, the aqueous leaching results in solutions of higher concentrations than those from the acid digestions. In all cases for which there were high concentrations of Na and K, the Cl⁻ content was always

adequate to account for the Na and K concentrations from the aqueous leach (assuming an alkali to halide ratio of 1:1).

Ion Chromatography of Aqueous Leach Solutions

Ion chromatographic analyses were performed only on the aqueous leach samples (Table 4). It was not possible to identify the anions of interest in the complexed dissolution samples because the high ionic strength of the solutions (12 M in NO_3^-) required that the samples be diluted to levels that resulted in $[\text{F}^-]$ and $[\text{Cl}^-]$ below the detection limit of the analytical method (and the fact that the digestion solutions contained F^- , one of the anions of interest).

All of the IC samples had nitrate concentrations below 1100 ppm, and all but three, R601285, H002088, and H002573, had levels below 900 ppm. These low values are indicative of the processing of these materials. These materials were calcined in air, at either 750 or 950 °C, for at least 2 hours or until the mass loss during heating was less than 0.5%.¹ Under these conditions, essentially all the nitrate salts present in these materials would most likely be converted to oxides. The few instances in which the nitrate concentration approached 0.1 wt% (1000 ppm) are most likely a result of a single factor, contamination, that occurred either during the aqueous leach process or while the solutions were handled subsequent to the leaching activities.

The generally low levels of phosphate are to be expected as well. The chemical processes associated with the 3013 materials, both at the production facilities where they were initially packaged and SRS, do not generally involve phosphates, so the low levels

observed for the majority of the samples (less than 1000 ppm) are expected. For the few cases where the phosphate concentrations might be above this level by IC (see Table 4), it should be noted that these results are related to “less than values” above 1000 ppm, so the high value is just an upper limit of the concentration and ought not be taken as a “measured” value due to the high detection limit associated with these measurements.

The generally low levels of sulfate are to be expected as well. The chemical processes associated with the 3013 materials, both at the production facilities where they were initially packaged and SRS, do not generally involve sulfates, so the low levels observed for the majority of the samples (less than 1000 ppm) are expected. For the few cases where levels above this value were detected, R610584 (1410 ppm), R610578 (4380 ppm), and H001941 (5100 ppm), the carbon-sulfur analyses of these three materials showed sulfur contents of 650 ppm, 1700 ppm, and 5100 ppm, respectively, indicating that the sulfate was probably present in the as-received material. It is likely that any differences between the IC and carbon-sulfur values for sulfur are related to sample heterogeneity.

The remaining two anions, F^- and Cl^- , are often present in these materials because of the utilization of halide salts in the high temperature processing of these materials.² The $[F^-]$ in two samples, H001941 (6220 ppm) and H001992 (3650 ppm), were above 1000 ppm; for these two samples F^- was the most abundant anion detected. The alkali metal contents of these two samples (as based on the ICP-ES results) are more than adequate to account for this much fluoride. In addition, the pre-surveillance prompt γ results (Table 7) for

these two samples indicate that there should be considerable fluorine present. It is not surprising that the IC results for fluoride show concentrations lower than might be expected.(Table 4) The primary reason for the low-biased $[F^-]$ is related not to the analytical technique, but to the generally low solubility of fluoride salts, especially the alkaline earth salts, as compared to the chloride analogues.

Numerous samples - R610735, R610697, R610298, R610324, R610578, H003409, H002573, H002534, H002750, H004111, and H002554 exhibited high $[Cl^-]$. In each of these cases, the prompt γ data from the PSDR and the cation results from the ICP-ES analyses supported the high $[Cl^-]$ result. It should be noted that the IC aqueous leaching results for Cl^- are more reliable than those for F^- . In general, the solubility of fluoride salts of alkali and alkaline earth metals (especially those in the upper half of the family) tend to be less soluble than the corresponding Cl^- salts because the fluoride ion has a greater charge density; therefore, the fraction of the fluoride sample dissolved during the leaching process is lower than that for the chloride salts.

ICP-MS and Radiochemical Results for Complexed Dissolution Samples

All of the complexed dissolution samples were subjected to both radiochemical analyses (alpha and gamma spectroscopy) and ICP-MS. In general, it is expected that the radiochemical analyses (with uncertainties of $\pm 10\%$ in the resulting values) give superior results for Pu because of the high specific activities of the Pu isotopes, while the ICP-MS method (with uncertainties of $\pm 20\%$ in the resulting values) produced superior results for ^{235}U , which is more difficult to quantify by radiochemical methods due to its low specific activity. Variations of the present results, as compared to the PSDR results, are not

surprising since the present results are the result of analyses performed on a small portion of the can contents, and the homogeneity of the samples cannot be verified. In general, the ICP-MS and radiochemical results from the present work were in agreement. There were inconsistencies between the ICP-MS and radiochemical analyses (particularly for samples R600719, H003157, and H002534); however, these discrepancies are random in nature, and they are probably related to sample handling errors, such as contamination, loss of material, and volume measurement errors.

SURFACE AREA ANALYSIS

The surface area of each sample was determined utilizing the Brunauer, Emmett and Teller (BET) method with nitrogen as the adsorbate. The analyzed materials were taken from the RP sample from each 3013 container. For each RP sample, two sub-samples were analyzed, and the surface area was taken to be the mean of the two values. The results show variation in surface area from a low of 0.21 m²/g to a high of 2.02 m²/g.

This wide variation of surface area is probably a reflection of the material properties of the samples. These materials were all calcined prior to being placed in the 3013 containers; however, the calcination temperatures were variable. Some materials were calcined at 750 °C, some at 950 °C, and two at undocumented temperatures. In addition, these materials are of variable composition, and it is not clear what impact the contaminants have on the measured surface areas. There appears to be little correlation of the observed surface area with any compositional or processing parameter other than calcination temperature, as can be seen on the plot of BET surface area versus calcination

temperature. (Figure 4) This plot does show surprising behavior of two samples, H003157 and H002088, which exhibit surface areas that are discordant with the rest of the set. The stabilization temperature for H003157 and H002088 are unknown, but the high surface areas suggest they may have been stabilized at a lower temperature than the remaining items. The high surface areas are not the only unique characteristics of these two materials. These two samples (H003157 and H002088) do not have a weapons grade Pu isotopic mixture; they have compositions that suggest they are reactor grade and fuel grade materials, respectively.

Comparison of Results to Pre-surveillance Data

Upon completion of the surveillance analyses, the experimental results are evaluated as to their reasonability. The most logical method of evaluation is to compare the present results to the data collected before the materials were packaged, and to any non-destructive evaluations performed on the packages. Probably the greatest single source of uncertainty in the measurements is sample homogeneity, or lack thereof. A wide range of materials are stored in 3013 containers, ranging from nearly pure PuO₂ to materials that are less than 50% PuO₂. Sampling of the mixtures has been performed in an attempt to choose “representative” samples of the stored materials, but it is not possible to determine how representative these samples are of the bulk material. Consequently, it is likely that the pre-surveillance results may be quite different than the present results for no reason other than the samples analyzed were not representative of the bulk materials. With these considerations in mind, an attempt to evaluate the agreement of the pre-surveillance and present measurements is presented.

ACTINIDE CONTENT

The most abundant actinide in the majority of these materials was Pu. In Table 7, the ICP-MS, radiochemistry, and pre-surveillance results for Pu are presented. In general, it appears that the ICP-MS under-estimates the actinide content, as compared to both the radiochemical and pre-surveillance results. This discrepancy is especially obvious in the first four items on the list. The radiochemical and pre-surveillance results appear to be in relatively good agreement for most of the items investigated, with the exception of H003157 and H002088 (as previously discussed in the Results and Discussion section).

One factor that can contribute to low Pu results is the sparingly small solubility of fluorides, specifically PuF₄ (and the related hydrated Pu-F phases). It is difficult to keep Pu in solution in the presence of fluoride. This inability to keep fluorides in solution is the reason why the most successful acid digestion technique applied during this investigation included the addition of H₃BO₃, a fluoride complexant, to the hot dissolver solution. However, even with the addition of the complexant, the presence of other solutes in the solution will reduce the solubility due to the fact that there is a limited amount of solute that can be dissolved in water. In addition, the presence of soluble chlorides will reduce the effectiveness of the complexant for keeping fluorides in solution by competing with the fluoride for the complexing species.

Overall, it appears that the radiochemical techniques utilized for this work produce results for Pu that are in good agreement with the pre-surveillance data with the exception of materials containing concentrations of ²⁴¹Pu at or above 1 weight %.

CHEMICAL COMPOSITION

Aqueous leaching and acid digestions were performed to produce aqueous solutions that can be used to assist in the determination of the composition of as-received materials.

The resulting solutions were analyzed and the results of the analyses were compared to the pre-surveillance and in-situ non-destructive analysis results. In Table 8 the prompt gamma results for Al, Be, Cl, F, Mg, and Na are presented for comparison with the IC (for F and Cl) and ICP-ES (for Al, Be, Mg, and Na) results. The detection limit for the IC and ICP analyses are in the 100 ppm range, while the prompt gamma detection limit is about 10 times less sensitive; however, in general, the results for Al and Be are in fairly good agreement. The Cl and Na results generally agree to within an order of magnitude, with the prompt gamma values generally higher than the ICP-ES. The results for F and Mg show very poor agreement. This disagreement is due to one significant factor, the generally poor solubility of fluorides, and the specifically poor solubility of MgF_2 .

MOISTURE CONTENT

An in-depth discussion of the moisture results for these materials is addressed in detail elsewhere in this issue;⁵ however, some general comments regarding how the TGA-MS moisture measurements performed at SRNL compare to the prepackaged moisture data are appropriate. The present moisture measurements were performed by monitoring m/z 17 and 18 signals as the sample temperature is increased from ambient temperature to 1000 °C; essentially all of the pre-surveillance values were based on mass-loss measurement of the samples when heated to 1000 °C. The present measurements are, in all but a few instances, lower than the pre-surveillance values: however, it is believed that

this discrepancy is most likely a function of the over-estimation of the moisture levels during the pre-surveillance measurements⁵ (as any evaporating species, included halide salts, were included in the mass loss attributed to moisture loss).

Conclusions

Twenty-eight samples were received and analyzed at SRNL in support of the 3013 DE Surveillance program. The samples were subjected to a battery of analyses in an attempt to characterize the phase and chemical character of the materials. Characterization techniques included: density determination; dissolution/leaching studies; ICP-MS, ICP-ES, and radiochemical analyses of dissolution products; IC and ICP-ES analyses of aqueous leachates; moisture content determination; surface area determination; and phase and elemental characterization by XRD and SEM, respectively.

The prepackaging treatment regimen was designed to remove liquids and other volatile reactive substances (such as excessive moisture) that might lead to degradation of the 3013 container during the 50-year design life. The purpose of the present investigation was to perform analyses to characterize the stored materials so that it will be possible to understand materials interactions involving the stored materials and the containers, and how the materials interactions impact the storage conditions. The purpose of the selected analyses was to characterize the chemical and phase composition of the stored materials. Radiochemical analyses used in tandem with ICP-MS provide a reliable approach to determining actinide content in these materials. The measured density of each item is in reasonable agreement with the density that is calculated from the linear combination of the “theoretical densities” of PuO₂ and NaCl or KCl. The digestion method utilized was

generally successful for dissolving the actinide-bearing materials, facilitating the use of standard analytical techniques to determine the cation content of these materials; however, for samples containing larger concentrations of halides, PuF₄ sometimes precipitated from the digested samples upon cooling. The precipitation of Pu-bearing phases impacts all of the wet chemistry results as the resulting solution do not provide a faithful representation of the solids (due to the loss of material through precipitation). The utilization of aqueous leaching facilitated the use of IC to determine the most important anion (Cl⁻) expected to be present in these materials. Knowledge about the chloride content of these materials is important since it is likely that any corrosion of the 3013 containers will be related to the presence of chloride salts. The present results do not provide a reasonable estimate of fluoride content of these materials. These poor results are primarily a result of the low solubility of fluorides in general, as compared to chlorides, and specifically the low solubility of CaF₂ and MgF₂. Development of a technique for digestion of fluoride salts is presently under consideration to remedy this shortcoming.

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⁵ Berg, J.M., M. L. Crowder, P. M. Almond. 2010. Relationship between Reported, As-Packaged Moisture and Moisture Measurements Made during Surveillance of 3013 Containers. *Journal of Nuclear Material Management* (this issue).

Acknowledgements

This work was performed at Savannah River National Laboratory. Savannah River National Laboratory is operated by Savannah River Nuclear Solutions for the US Department of Energy under contract DE-AC09-08SR22470.

Figure 1 Sample H002509 after removal from the 3013 inner can. This material contains approximately 70% actinides by weight.



Figure 2 Sample H001992 after removal from the 3013 inner can. The small blue and whitish flecks are indicative of material that might be sampled and designated as 'if required' samples. This material contains approximately 52% actinides by weight.



Figure 3 Experimentally measured sample density plotted as a function of pre-surveillance data report actinide content.

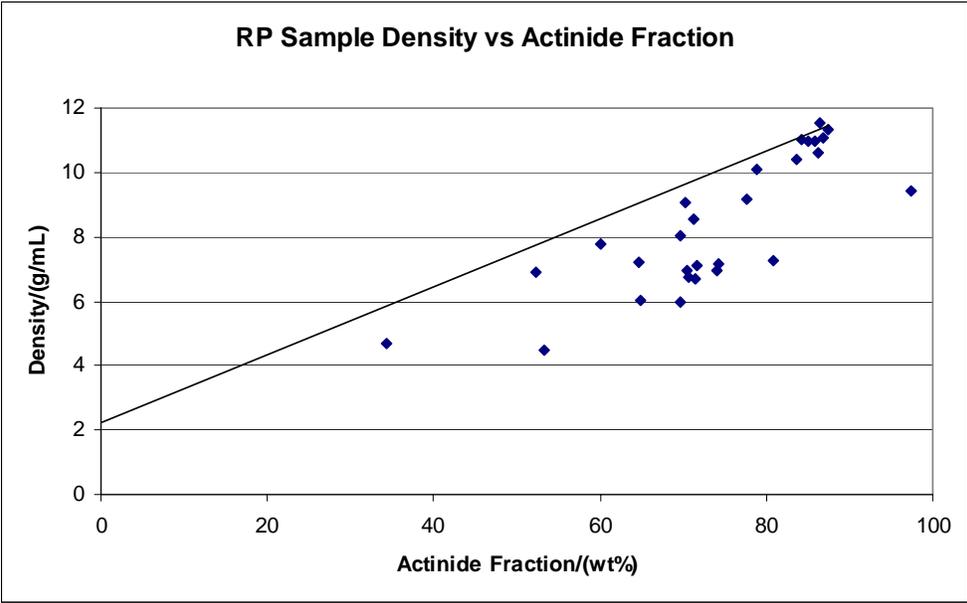


Figure 4 Plot of BET surface area versus calcination temperature for selected items.

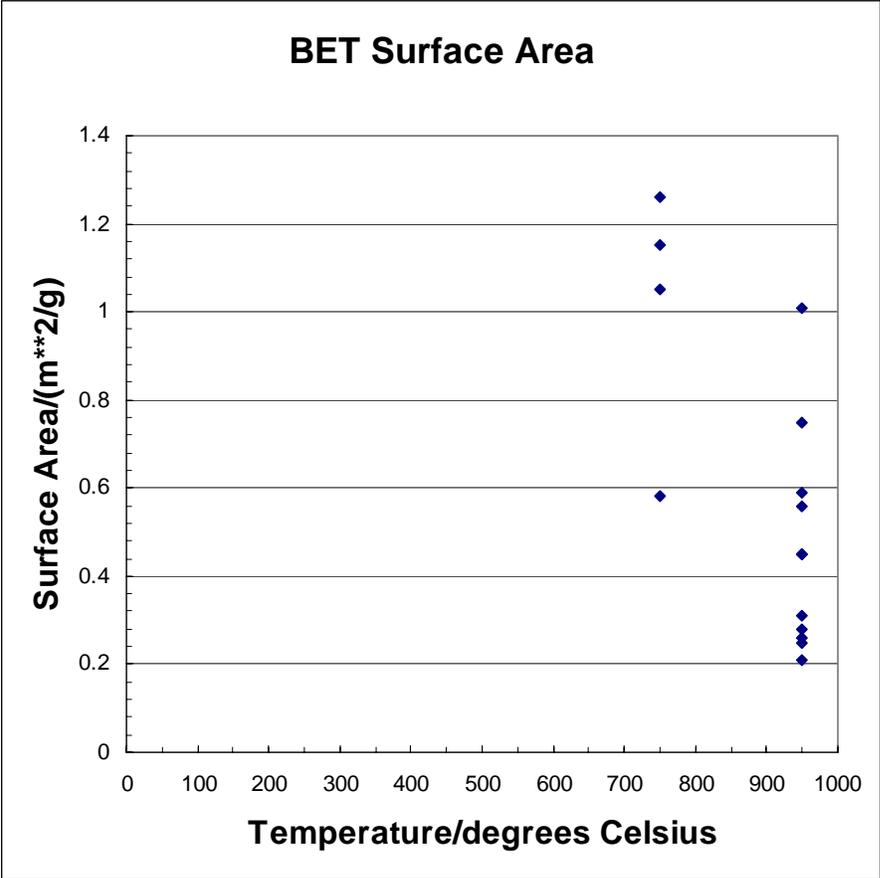


Table 1 Sample Characteristics

Sample	³Actinide Content/(wt%)	$\rho/\text{g/cm}^3$	¹Phases Identified by XRD	⁴Moisture/wt%	Surface Area/(m²/g)	²Storage Atmosphere
R600885	86.42	11.56	PuO ₂ , NiCr ₂ O ₄	0.05	0.94	89% He, 10% N ₂ , 0.1% O ₂ , trace H ₂ , trace CO ₂
R601722	84.25	11.00	PuO ₂ , NiCr ₂ O ₄ , NiO, Cr ₂ O ₃ , AgCl	0.04	0.58	82% He, 16% N ₂ , less than 0.1% O ₂ , trace H ₂
R601957	87.48	11.32	PuO ₂ , NiCr ₂ O ₄ , NiO, (Fe,Mg)(Cr,Fe) ₂ O ₄	0.04	0.47	86% He, 12% N ₂ , trace H ₂ , trace CO ₂
R600719	86.24	10.62	PuO ₂ , Al ₂ O ₃ , NiO, NiCr ₂ O ₄	0.04	0.82	80% He, 18% N ₂ , trace H ₂ , trace CO ₂
R610735	53.35	4.28	PuO ₂ , KCl, NaCl, NiO, MgO, Fe ₃ O ₄ , Na _{0.1} K _{0.9} Cl, PbO ₂ , Na _{0.68} Fe _{0.68} Si _{0.32} O ₂	0.19	0.58	76% He, 19% N ₂ , trace H ₂ , 0.2% CO ₂
R610697	69.76	5.88	PuO ₂ , KCl, NaCl, NiO, Na _{0.1} K _{0.9} Cl	0.14	0.58	81% He, 19% N ₂ , trace H ₂ , trace CO ₂ , trace CH ₄
R601285	85.84	10.95	PuO ₂	0.1	0.99	75% He, 24% N ₂ , trace H ₂ , trace CO ₂ , less than 0.1% CH ₄
R602731	97.43 ³	9.42	PuO ₂ , U ₃ O ₈	0.03	0.26	81% He, 19% N ₂
R601318	83.62	10.41	PuO ₂ , NiCr ₂ O ₄	0.02	0.75	88% He, 11% N ₂
H000898	77.68	9.15	PuO ₂ , NiCr ₂ O ₄ , SiO ₂ (Q), SiO ₂ (Cr), Cr ₂ O ₃ , Fe/Ni Alloy, Graphite	0.04	0.25	76% He, 23% N ₂
R610327	80.76 ³	7.24	PuO ₂ , U ₁₃ O ₃₄ , UO ₂ , (U,Pu)O _(2-x) , KCaF ₃	0.04	1.01	78% He, 20% N ₂
R610298	64.83	6.03	PuO ₂ , NiO, KCl, NaCl, Na _{0.1} K _{0.9} Cl, NiCr ₂ O ₄	0.14	0.31	79% He, 18% N ₂
R610324	71.55	6.69	PuO ₂ , KCl, NaCl, NiO	0.10	0.58	79% He, 21% N ₂
H001992	52.30	6.89	PuO ₂ , Fe ₂ O ₃ , NiO, NiCr ₂ O ₄ , SiO ₂ (Cr), ThO ₂	0.03	0.45	54% He, 43% N ₂

Sample	³ Actinide Content/(wt%)	$\rho/\text{g}/\text{cm}^3$	¹ Phases Identified by XRD	⁴ Moisture/wt%	Surface Area/(m ² /g)	² Storage Atmosphere
H003157	84.98	10.96	PuO ₂ , NiO, NiCr ₂ O ₄	0.10	1.98	52% He, 46% N ₂ , 1.6% O ₂
R610584	71.35	8.54	PuO ₂ , SiO ₂ (Q)	0.07	0.21	81% He, 18% N ₂ , 0.6% CO ₂
R610578	64.70	7.22	PuO ₂ , NaCl, CaWO ₄ , Ca ₂ Ta ₂ O ₇	0.19	0.56	78% He, 21% N ₂
H001916	34.26	4.96	PuO ₂ , Fe ₂ O ₃ , NiCr ₂ O ₄ , Ca ₂ Ta ₂ O ₇ , WO ₃ , Mg ₂ Si ₅ Al ₄ O ₈ , WNiO ₄ , Ta ₁₆ W ₁₈ O ₉₄ , K ₆ NiW ₉ O ₃₁ , Na _{0.5} Cr _{0.5} WO ₄ , SiO ₂ (Cr)	0.07	0.28	52% He, 49% N ₂
H002088	86.74	11.07	PuO ₂ , NiCr ₂ O ₄	0.18	2.02	57% He, 44% N ₂
H003409	73.96	6.97	PuO ₂ , NaCl, KCl	0.24	1.05	46% He, 38% N ₂ , 18% H ₂
H002573	74.27	7.17	PuO ₂ , KCl, NaCl	0.33	1.26	41% He, 35% N ₂ , 29% H ₂
H002534	70.49	6.96	PuO ₂ , KCl, NaCl, NiCr ₂ O ₄	0.19	1.15	40% He, 29% N ₂ , 30% H ₂ , 2.6% CO ₂
R610679	70.35	9.06	PuO ₂ , C, KFe(WO ₄) ₂ , (W,Fe)(O,OH) ₂ , CaF ₂	0.03	0.45	66% He, 31% N ₂ , 2.8% CO ₂
H002750	69.63	8.06	PuO ₂ , NiCr ₂ O ₄ , Na _{0.35} Fe _{0.65} Ti _{3.34} O ₈ , NaAlSiO ₄ , (K,Na)AlSiO ₄	0.07	0.59	59% He, 41% N ₂
H004099	78.88	10.12	PuO ₂ , NiCr ₂ O ₄ , Fe ₂ O ₃ , MgO	0.03	0.46	41% He, 55% N ₂ , 0.19% O ₂ , trace H ₂ , 0.34% CO ₂ , trace CO, 1.3% N ₂ O
H004111	71.75	7.13	PuO ₂ , NiO, NaCl, KCl, NiCr ₂ O ₄	0.26	1.00	32% He, 48% N ₂ , less than 0.1% O ₂ , 20% H ₂ , trace CO ₂ , trace CO, less than 0.1% N ₂ O
H002554	70.59	6.76	PuO ₂ , NiCr ₂ O ₄ , NaCl, KCl	0.22	1.07	Pressure too low to measure gas composition

Sample	³ Actinide Content/(wt%)	$\rho/\text{g/cm}^3$	¹ Phases Identified by XRD	⁴ Moisture/wt%	Surface Area/(m ² /g)	² Storage Atmosphere
H001941	60.08	7.81	PuO ₂ , NiCr ₂ O ₄ , NiO, Cr ₂ O ₃ , SiO ₂ (Cr)	0.02	0.35	49% He, 50% N ₂ , trace H ₂ , trace CO ₂ , trace CO, less than 0.1% N ₂ O

¹(Cr) – cristobalite, (Q) – quartz

²Composition in volume percent.

³Composition estimated from gamma counting. The uncertainty in the measurement of U by this technique is quite large because U-235 has only a single gamma which can be utilized.

⁴Moisture of sample taken from 3013 can when can was initially opened.

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Table 2 Bulk and Pycnometer Densities for 3013 Representative Samples

Sample	Bulk ρ/(g/mL)	Pycnometer ρ/(g/mL)	Bulk ρ/ Pycnometer ρ
R600885	2.1	11.56	0.18
R601722	2.4	11.00	0.22
R601957	4.3	11.34	0.38
R600719	2.8	10.62	0.26
R610735	2.4	4.5	0.53
R610697	2.4	5.95	0.40
R601285	2.4	10.95	0.22
R602731	2.2	9.42	0.23
R601318	2.4	10.41	0.23
H000898	3.0	9.15	0.33
R610327	2.6	7.24	0.36
R610298	2.6	6.03	0.43
R610324	2.4	6.69	0.36
H001992	2.3	6.89	0.33
H003157	2.5	10.96	0.23
R610584	2.6	8.54	0.30
R610578	2.2	7.22	0.30
H001916	1.7	4.69	0.36
H002088	2.5	11.07	0.23
H003409	2.3	6.97	0.33
H002573	2.5	7.17	0.35
H002534	2.4	6.96	0.34
R610679	2.3	9.06	0.25
H002750	2.4	8.06	0.30
H004099	2.4	10.09	0.24
H004111	2.4	7.13	0.34
H002554	2.3	6.76	0.34
H001941	2.2	7.80	0.28
R600885	2.1	11.56	0.18

Table 3 Dissolution Residues

Sample ID	Uncomplexed Dissolution, % Insoluble	Insoluble Phases Identified by XRD, Uncomplexed Dissolution	Complexed Dissolution, % Insoluble	Insoluble Phases Identified by XRD, Complexed Dissolution
R600885		PuO ₂ , Pu ₃ F ₁₂ ·H ₂ O		Pu ₃ F ₁₂ ·H ₂ O*
R601722		Pu ₃ F ₁₂ ·H ₂ O**		None
R601957		None		Pu ₃ F ₁₂ ·H ₂ O*
R600719		Pu ₃ F ₁₂ ·H ₂ O*		None
R610735		NiCr ₂ O ₄ , NaCl, MgWO ₄ , NiO		NiO
R610697		Pu ₃ F ₁₂ ·H ₂ O*		Pu ₃ F ₁₂ ·H ₂ O*
R610285		PuO ₂ , Pu ₃ F ₁₂ ·H ₂ O		None
R602731	58.7	PuO ₂ , Pu ₃ F ₁₂ ·H ₂ O	0	None*
R601318	0	None	1.4	None*
H000898	25.8	Pu ₃ F ₁₂ ·H ₂ O	4.8	None*
R610327	6.4	None	2.7	None
R610298	59.1	PuF ₄ , PuF ₄ (H ₂ O) _{1.6}	3.1	PuF ₄ (H ₂ O) _{1.6}
R610324	26.9	PuO ₂ , PuF ₄ , PuF ₄ (H ₂ O) _{1.6}	2.7	PuO ₂ , PuF ₄ , PuF ₄ (H ₂ O) _{1.6} *
H001992	68.3	Pu ₃ F ₁₂ ·H ₂ O, (Fe,Mg)(Cr,Fe) ₂ O ₄	26.1	(Fe,Mg)(Cr,Fe) ₂ O ₄ , NiO
H003157	54.0	Pu ₃ F ₁₂ ·H ₂ O	0	None*
R610584	27.7	Pu ₃ F ₁₂ ·H ₂ O	4.6	KNiCrF ₆ , graphite, MgCrF ₆ , SiC
R610578	41.2	Pu ₃ F ₁₂ ·H ₂ O, WO ₃ ·H ₂ O	25.0	Pu ₃ F ₁₂ ·H ₂ O, WO ₃ ·H ₂ O, PuO ₂
H001916	11.5	Fe ₂ O ₃ , SiO ₂ , NiCr ₂ O ₄ , (Na,Ca,U) ₂ (Nb,Ta) ₂ (OH,F)O ₆ *	21.8	Fe ₂ O ₃ , SiO ₂ (Q), MgWO ₄ , NiCr ₂ O ₄ , (Na,Ca,U) ₂ (Nb,Ta) ₂ O ₆ (OH,F), NaTi _{0.2} Nb _{0.8} O _{2.9}
H002088	61.2	Pu ₃ F ₁₂ ·H ₂ O	0.4	None
R610700	36.3	Pu ₃ F ₁₂ ·H ₂ O	0.1	Pu ₃ F ₁₂ ·H ₂ O, WO ₃ ·H ₂ O, PuO ₂ *
H002573	38.7	PuF ₄ (H ₂ O) _{1.6} , PuF ₄	9.6	Trace PuF ₄ (H ₂ O) _{1.6} , PuF ₄ and PuO ₂
H002534	37.8	PuF ₄ (H ₂ O) _{1.6} , PuF ₄	0.8	NiCr ₂ O ₄ , NiO, Cr ₂ O ₃
R610679	67.8	Pu ₃ F ₁₂ ·H ₂ O	6.8	TaO ₂ , Ta ₂ O ₅
H002750	52.3	Pu ₃ F ₁₂ ·H ₂ O	7.1	Fe ₂ O ₃ , NiCr ₂ O ₄ ¹
H004099	88.2	PuF ₄ (H ₂ O) _{1.6}	2.2	NiO, NiCr ₂ O ₄ , Fe ₂ O ₃
H004111	73.0	PuF ₄ (H ₂ O) _{1.6} , PuF ₄ , K ₃ NiF ₆	4.5	WO ₃ ·H ₂ O*
H002554	46.3	Pu ₃ F ₁₂ ·H ₂ O, (K,Na)(Al,Mg,Fe) ₂ Si _{3.1} Al _{0.9} O ₁₀ (OH) ₂	4.4	PuO ₂ , PuF ₄ *
H001941	62.1	NiO, Cr ₂ O ₃ , NiCr ₂ O ₄ , Pu ₃ F ₁₂ ·H ₂ O, Na ₂ UO ₂ W ₂ O ₈ , CaWO ₄	21.6	NiO, Cr ₂ O ₃ , NiCr ₂ O ₄ , SrCa _{0.5} W _{0.5} O ₃

* Polytetrafluoroethylene and SiO₂, constituents of the filter media, were detected.
** Polytetrafluoroethylene, a constituent of the filter media, was detected.
¹ Unidentified material, face-centered cubic, a=3.94 Å.

Table 4 IC Anion Results from Aqueous Leach Solutions

Sample	F⁻ /(µg/g_{sample})	Cl⁻ /(µg/g_{sample})	NO₃⁻ /(µg/g_{sample})	PO₄³⁻ /(µg/g_{sample})	SO₄²⁻ /(µg/g_{sample})
R600885	555	118	875	<1400	134
R601722	498	355	785	<1250	225
R601957	<500	<500	890	1250	<500
R600719	<500	<500	825	1250	<1250
R610735	166	200000	469	930	831
R610697	<600	100000	530	515	655
R601285	<600	316	928	600	<600
R602731	<438	<438	638	<1090	<438
R601318	<465	<465	656	<1160	<465
H000898	393	<451	535	<1130	<451
R610327	339	518	<369	<747	763
R610298	<303	98000	<303	<758	712
R610324	<300	76000	<300	<749	<488
H001992	3650	322	<304	<761	795
H003157	<161	<161	850	<161	220
R610584	361	1860	180	<150	1410
R610578	<157	41000	187	<157	4380
H001916	<175	301	<159	849	434
H002088	<150	150	975	<150	225
H003409	<150	52000	209	<150	388
H002573	<157	67000	1080	<157	376
H002534	<152	64000	286	<152	646
R610679	300	<151	300	<151	330
H002750	814	1720	256	<302	783
H004099	<157	<157	313	376	250
H004111	<150	58100	210	<150	436
H002554	<151	65600	210	No Result	480
H001941	6220	516	212	167	1320

Table 5 ICP-ES Cation Results from Aqueous Leach.

Cation Concentrations/($\mu\text{g/g}_{\text{sample}}$)													
Sample	Ag	Al	Ba	Be	Ca	Cd	Cr	Fe	K	Mg	Na	Ni	Pb
R600885	< 10.6	< 11.3	6.1	< 0.1	265	< 1.4	13.4	< 3.1	< 53.2	13	< 56.5	14	< 9.2
R601722	< 11.3	24.7	< 1.3	12.9	114.6	< 1.1	< 2.3	< 3.3	128.5	153.0	403.5	76.2	< 9.7
R601957	< 3.6	< 12.7	3.5	< 0.14	227	< 1.0	< 1.3	< 2.0	< 59.9	33.6	59.3	38.8	< 10.3
R600719	< 3.4	< 12	< 0.74	0.6	22.7	< 13.4	< 13.5	< 13.8	< 37.4	18.7	164.5	19.1	< 17.2
R610735	28.4	ND	5.4	1.3	428	< 3.8	17	< 8.5	76200	7160	47400	584	< 25.3
R610697	< 25.7	ND	< 1.63	< 0.30	< 31.1	< 3.23	6.7	< 7.46	60900	5180	37100	30.4	< 22.1
R601285	< 31.2	< 42.7	< 2.0	< 0.8	< 32.1	< 4	< 3.4	< 9.1	< 156	< 31.7	376.5	21.9	< 26.9
R602731	< 1.23	ND	< 0.668	0.2335	4.285	< 0.795	< 0.878	< 1.36	< 51.6	1.965	12.4	10.9	< 4.52
R601318	36.25	ND	0.9955	0.0771	253.5	< 0.845	< 0.934	< 1.44	< 54.8	90.4	48.7	20.8	< 5.00
H000898	< 1.09	ND	< 1.04	< 0.065	462.5	< 1.48	< 0.907	< 1.34	< 53.2	53.6	46.25	18.55	< 4.86
R610327	< 0.723	ND	< 0.687	50.35	322.5	< 0.543	< 0.600	< 0.926	77.45	22.1	51.3	54.8	< 3.22
R610298	2.385	ND	2.62	0.236	467.5	< 1.38	< 1.73	< 2.35	49650	2045	30400	1995	43.95
R610324	< 1.81	ND	< 1.72	< 0.0474	< 2.33	< 1.36	26.75	< 2.32	41150	3150	24800	8.83	< 8.07
H001992	3.47	ND	< 1.16	8.37	109.5	< 1.38	8.29	< 2.35	640.5	767	3060	8.63	< 8.17
H003157	< 1.56	ND	< 0.985	< 0.0930	71.75	< 1.17	< 1.37	< 2.00	< 76.0	25.7	47.45	207.5	< 6.94
R610584	< 1.45	ND	4.815	46.15	1265	< 1.09	< 1.20	< 1.86	137.5	106	204	65.9	< 6.45
R610578	< 3.78	ND	7.885	< 0.300	19200	< 2.84	92.3	< 4.85	4675	304	2820	9.065	< 16.8
H001916	< 1.53	ND	< 1.46	< 0.0916	8.065	< 1.15	254	< 1.97	< 74.9	294	2780	< 14.1	< 6.83
H002088	< 1.45	ND	< 0.690	< 0.433	30.1	< 0.698	< 0.603	4.5	< 35.4	22.95	90.35	42.7	< 3.23
H003409	< 1.45	ND	< 0.916	< 0.865	175	< 0.379	24.6	< 1.38	26099.5	1670	15300	< 13.3	< 6.45
H002573	< 12.5	ND	< 0.954	< 3.79	2.545	< 1.45	27.6	< 1.44	33300	1510	20050	< 13.9	< 6.72
H002534	< 5.95	ND	< 0.924	< 1.21	73.45	< 1.10	17.3	< 1.60	33850	1830	19050	< 13.4	< 6.40
R610679	< 3.03	ND	5.52	3.505	211	< 0.624	< 1.79	< 0.429	< 52.4	30.75	44.65	184.5	< 6.32
H002750	< 1.68	ND	0.719	< 0.928	41.05	< 12.1	1610	< 0.704	8270	151.5	2090	< 121	< 6.32
H004099	< 1.74	ND	< 0.655	< 0.937	248.95	< 0.463	16.2	< 0.443	71.75	277.5	135.5	< 8.13	< 6.53
H004111	< 1.67	ND	< 0.629	< 0.0920	499.5	< 0.347	169	< 0.425	30150	840	18100	519	< 6.27
H002554	< 1.67	ND	< 1.20	< 0.900	4.29	< 0.444	31.65	< 0.425	35900	1460	20900	< 7.80	< 6.27
H001941	< 12.2	ND	< 0.312	59.8	14.1	< 0.629	48.5	< 1.29	1300	46.8	4735	98.75	< 6.37

Table 6 ICP-ES Cation Results from Complexed Dissolution

Sample	Cation Concentrations/($\mu\text{g/g}_{\text{sample}}$)												
	Ag	Al	Ba	Be	Ca	Cd	Cr	Fe	K	Mg	Na	Ni	Pb
R600885	<0.163	<0.652	<163	<12.2	779	<163	170	1120	<706	<163	<326	804	<85.2
R601722	<318	<636	<159	<159	1179.5	<159	<159	1095	<689	399	958	2180	<83.1
R601957	<164	<328	<164	<12.3	576.5	<164	<164	<492	<711	<164	343.5	627.5	<164
R600719	<163	<326	<55.0	<163	<163	<163	<163	953.5	<542	<163	<542	969.5	<163
R610735	<159	<1.59e3	<159	2010	621.5	<159	921.5	3755	72550	17600	46050	9000	<159
R610697	<198	<2015	<54.7	<5.22	<163	<96.2	707.5	948.5	44400	11000	27900	9660	<111
R601285	<164	<684	<55.4	<164	<165	<97.4	<328	781.5	<545	<16.4	443.5	575	<164
R602731	<22.8	<66.8	<18.0	<11.3	<16.1	<18.2	<15.8	299	<925	<7.00	<85.7	345	<84.4
R601318	<240	2440	<18.4	<48.5	5170	<18.6	<160	2490	<943	1260	<87.3	911	<86.0
H000898	<191	2900	<17.9	<47.3	13300	<18.1	<312	3590	<919	3380	<312	1080	<83.9
R610327	<780	<780	<156	10000	4680	<18.1	446	7420	<1500	462	<690	1210	<156
R610298	<159	<1590	<12.1	<159	544	<14.4	769	4330	40800	8890	26000	5850	717
R610324	<322	<1720	<12.3	<11.6	154	<18.7	245	765	41600	8820	26600	8080	<86.6
H001992	<166	3590	<166	<166	6330	<166	439	12500	1530	27900	10500	11000	<332
H003157	<178	<2810	<178	<178	218	<178	<178	2160	<255	<356	368	2160	<178
R610584	<19.9	2670	<165	3480	12900	<165	418	6710	<972	2580	946	1050	<825
R610578	<180	<900	<180	1830	45000	<20.9	461	3580	3610	5480	3480	4300	<180
H001916	<1708	23500	62.3	49.2	2050	<170	4110	23600	1610	26300	25700	4950	<170
H002088	<167	<334	<167	<167	232	<8.61	<163	590	<239	<167	311	415	<167
H003409	<165	<330	<165	<16.5	815	<16.5	144	1020	29900	6940	18200	1930	<86.2
H002573	<168	<1260	<12.8	<50.9	137	<19.5	39.4	1230	28600	4380	18400	4300	<90.3
H002534	<78.5	<1570	<12.0	<15.7	381	<14.3	1090	5980	29900	7920	17900	17600	<84.4
R610679	<330	<3300	<165	<165	10200	<8.50	676	3030	<715	776	<629	3190	<86.2
H002750	<161	11000	106	195	1520	<161	2890	11800	9780	3710	8360	8280	119
H004099	<165	<825	<320	<12.4	1230	<165	802	7600	<715	4220	<330	2660	<165
H004111	<163	<326	<163	<163	1220	<163	1070	1950	26800	6060	17100	8840	<85.2
H002554	<159	<398	<159	<11.9	<159	<159	1210	4030	34400	6660	20700	15900	<83.1
H001941	52	5940	<163	111	2040	<163	280	546	2790	1330	7680	9490	1690

Table 7 Pu concentrations from ICP-MS, radiochemical analyses (γ and α scans) of complexed dissolution products, and PSDR; ^{241}Am concentrations from radiochemical analyses (γ and α scans) of complexed dissolution products and PSDR

Sample	[Pu]/(wt%)			Pu Isotopic Fractions/(isotopic %)				^{241}Am /(wt%)		
	ICP-MS	γ and α scan	PSDR	^{238}Pu	^{239}Pu	^{240}Pu		^{241}Pu	γ scan	PSDR
γ scan				γ scan	γ scan	PSDR	γ scan			
R600885	57.68	57.20	86.42	0.01	93.80	6.07	5.92	0.13	0.18	0.16
R601722 ¹	59.53	66.51	84.05	0.01	93.70	6.12	5.75	0.12	0.17	0.16
R601957	55.18	67.98	87.48	0.01	94.40	5.43	5.74	0.12	0.15	0.13
R600719 ²	56.24	79.52	84.93	0.01	94.50	5.31	5.68	0.13	0.14	0.16
R610735	47.06	50.19	53.35	0.01	93.30	6.56	6.05	0.09	0.11	0.11
R610697	68.27	77.93	69.76	0.01	94.10	5.83	6.04	0.08	0.10	0.09
R601285	84.97	86.43	85.84	0.02	94.10	5.72	6.10	0.14	0.22	0.18
R602731 ³	73.17	65.08	55.86	0.01	93.90	5.94	5.68	0.10	0.21	0.09
R601318	72.69	84.11	83.46	0.01	93.70	6.15	5.56	0.12	0.18	0.16
H000898	71.96	79.73	77.52	0.01	93.80	6.02	6.05	0.12	0.20	0.17
R610327 ⁴	11.56	12.71	14.73	0.01	94.30	5.53	6.32	0.10	0.03	0.03
R610298	57.27	58.31	64.71	0.01	93.90	5.97	5.94	0.09	0.12	0.12
R610324	70.44	80.06	71.45	0.01	94.10	5.75	5.89	0.07	0.11	0.10
H001992	45.30	35.97	52.30	0.02	93.00	6.82	6.57	0.12	0.17	0.21
H003157	35.77	67.04	81.06	0.31	75.90	21.40	22.21	0.97	3.68	3.92
R610584	70.98	68.63	71.21	0.01	93.70	6.16	6.60	0.12	0.16	0.14
R610578	42.78	54.44	64.54	0.01	93.70	6.17	5.76	0.11	0.12	0.16
H001916	34.80	32.52	34.07	0.01	94.30	5.58	5.68	0.10	0.09	0.09
H002088	77.27	71.39	81.29	0.53	80.40	16.50	17.47	1.33	5.37	5.46
H003409	67.96	83.69	73.84	0.01	94.30	5.61	5.78	0.07	0.0001	0.12
H002573	72.81	65.18	74.19	0.01	94.50	5.19	5.52	0.06	0.08	0.08
H002534	54.00	78.32	70.40	0.01	94.30	5.66	5.78	0.06	0.10	0.10
R610679 ⁵	58.68	75.47	59.86	0.01	94.40	5.48	6.03	0.12	0.15	0.14
H002750	65.16	85.28	69.63	0.01	93.80	5.97	6.15	0.15	0.22	0.20
H004099	68.14	83.41	78.60	0.02	93.60	6.11	5.94	0.22	1.00	0.28
H004111	64.44	71.88	71.64	0.01	94.50	5.45	5.74	0.07	0.11	0.11

Sample	[Pu]/(wt%)			Pu Isotopic Fractions/(isotopic %)				[²⁴¹ Am]/(wt%)		
				²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu				²⁴¹ Pu
	ICP-MS	γ and α scan	PSDR	γ scan	γ scan	γ scan	PSDR	γ scan	γ scan	PSDR
H002554	66.65	83.31	70.49	0.01	94.20	5.71	5.73	0.07	0.11	0.10
H001941	53.84	55.81	59.69	0.04	91.80	7.82	7.68	0.28	0.44	0.39
1 [U]=0.20% (93.12% ²³⁵ U) 2 [U]=1.31% (93.15% ²³⁵ U) 3 [U]=41.48% (92.80% ²³⁵ U) 4 [U]=66.01% (93.16% ²³⁵ U) 5 [U]=10.35% (93.16% ²³⁵ U)										

Table 8 Comparison of Elemental Concentrations from PSDR Prompt γ Results and DE Chemical Analyses

Sample	Elemental Concentrations/($\mu\text{g}/\text{g}_{\text{sample}}$)											
	Al ¹		Be ¹		Cl ²		F ²		Mg ¹		Na ²	
	PSDR	ICP	PSDR	ICP	PSDR	ICP	PSDR	ICP	PSDR	ICP	PSDR	ICP
R600885	ND	<0.652	ND	<12.2	ND	118	ND	555	ND	<163	ND	< 56.5
R601722	ND	<636	ND	<159	ND	355	2800	498	200	399	500	403.5
R601957	ND	<328	ND	<12.3	ND	<500	ND	<500	ND	<164	ND	59.3
R600719	ND	<326	ND	<163	ND	<500	ND	<500	ND	<163	ND	164.5
R610735	ND	<1.59e3	700	2010	61400	200000	ND	166	ND	17600	24300	47400
R610697	ND	<2015	ND	<5.22	61700	100000	ND	<600	6700	11000	25100	37100
R601285	ND	<684	200	<164	ND	316	ND	<600	100	<16.4	ND	376.5
R602731	ND	<66.8	ND	<11.3	ND	<438	ND	<438	500	<7.00	ND	12.4
R601318	2500	2440	ND	<48.5	ND	<465	7300	<465	1000	1260	200	48.7
H000898	ND	2900	ND	<47.3	ND	<451	14000	393	5200	3380	ND	46.25
R610327	ND	<780	ND	10000	ND	518	ND	339	ND	462	N D	51.3
R610298	ND	<1590	ND	<159	66300	98000	ND	<303	6000	8890	29300	30400
R610324	ND	<1720	ND	<11.6	72500	76000	ND	<300	6400	8820	28700	24800
H001992	4800	3590	ND	<166	ND	322	27300	3650	5500	27900	6800	3060
H003157	2600	<2810	ND	<178	ND	<161	10900	<161	500	<356	200	47.45
R610584	ND	2670	4800	3480	ND	1860	11700	361	27000	2580	ND	204
R610578	ND	<900	1100	1830	38400	41000	14200	<157	6500	5480	2500	2820
H001916	11800	23500	ND	49.2	ND	301	3800	<175	13100	26300	20100	2780
H002088	ND	<334	ND	<167	ND	150	ND	<150	4000	<167	4000	90.35
H003409	ND	<330	ND	<16.5	60900	52000	ND	<150	9300	6940	23600	15300
H002573	ND	<1260	ND	<50.9	61500	67000	ND	<157	6800	4380	24500	20050
H002534	ND	<1570	ND	<15.7	71800	64000	ND	<152	10600	7920	36000	19050
R610679	4300	<3300	ND	<165	ND	<151	9100	300	1800	776	ND	44.65
H002750	6500	11000	700	195	3500	1720	1700	814	2800	3710	4100	2090
H004099	ND	<825	ND	<12.4	58000	<157	ND	<157	9600	4220	19200	135.5
H004111	ND	<326	ND	<163	79500	58100	ND	<150	10700	6060	35700	18100
H002554	ND	<398	ND	<11.9	58700	65600	ND	<151	8300	6660	25100	20900
H001941	6000	5940	500	111	ND	516	8100	6220	900	1330	3500	4735

- | | |
|---|---|
| 1 | Data from complexed acidic dissolution. |
| 2 | Data from aqueous leach. |
| 3 | ND – not detected |