

**Lab-Scale Demonstration of Plutonium Purification
by Anion Exchange, Plutonium(IV) Oxalate
Precipitation, and Calcination to Plutonium Oxide to
Support the MOX Feed Mission**

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August 2012

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contract number DE-AC09-08SR22470.



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EXECUTIVE SUMMARY

To support the upcoming mission to produce feed for the Mixed Oxide (MOX) Fuel Fabrication Facility, this study included a demonstration of the anion exchange, precipitation and calcination steps expected for the HB-Line process. Specifically, an anion exchange column experiment produced 1.76 L of purified 44.8 g/L plutonium (Pu) solution at 1.23 M free acid. After increasing the acidity to 1.54 M, researchers performed two batches of Pu(IV) oxalate precipitation at 50 °C using precipitation times expected in HB-Line. The resulting two batches of Pu oxalate were calcined separately at 650 °C for nominally four hours to yield plutonium dioxide (PuO₂). During calcination, a flow of air passed through the furnace.

Replicate samples of PuO₂ from the Demo 1 batch, which had limited exposure to humid air, showed TGA mass losses of 0.33-0.34 wt % when heated to 1000 °C. Mass spectrometry evaluation of these samples indicated moisture contents of 0.30 – 0.32 wt %. Exposing Demo 1 material to humid air (44 – 60% relative humidity [RH]) for four days yielded material that likely contained ~0.6 wt % moisture.

Subsequent studies with Demo 1 sample portions exposed to humid air showed that placing the PuO₂ in a stream of dry argon gas for 1 hour caused release of significant amounts of moisture. Testing achieved a moisture loss of 0.26 wt % at room temperature and 0.44 wt % at ~93 °C. Assuming an estimated starting moisture content of ~0.6 wt %, this preliminary study suggests that the use of a dry argon purge may be sufficient to achieve the required moisture content of <0.50 wt %. Unfortunately, a TGA instrument problem occurred that prevented the confirmation that the remaining moisture content in the samples purged with argon was <0.50 wt %. Though the argon purge results are attractive for sample sizes of ~1 g, further studies are needed to assess the feasibility of purging batches of 1 kg or more with dry gas and the conditions needed to consistently attain <0.50 wt % moisture.

During normal TGA-MS operations, the Demo 1 sample characteristics were consistent with an earlier study of small-scale samples produced via similar conditions. In both cases, the bulk of the moisture released from samples by 300 °C, as did a significant portion of the carbon dioxide (CO₂). As with earlier samples, the Demo 1 material released a minor amount of nitric oxide (NO) in the ~40-300 °C range, but did not release carbon monoxide (CO) or sulfur dioxide (SO₂).

Both batches of PuO₂ produced in this study exhibited good purity. In the oxide product there were five elements that may exceed the limit for MOX oxide feed – gadolinium (Gd), potassium (K), molybdenum (Mo), phosphorus (P), and silicon (Si). Of these, four of the analyte (K, Mo, P, and Si) measurements were below the method detection limit. Therefore, only Gd was positively detected above the limit. Of the five elements that exceeded the limit in the oxide product, four of them (K, Mo, P, and Si) are also above the limit in the Pu feed solution to precipitation. However, in all four cases, the concentrations in the Pu feed solution were also below the measurement detection limit. Of the four elements (K, Mo, P, and Si) that exceed the oxide product limit while being below the method detection limits, none of them are expected to be retained by the anion exchange column, nor are they expected to precipitate with oxalic acid. Consequently, based on process knowledge and the absence of data positively confirming that K, Mo, P, and Si were above the limit, it is likely that they were below the limit. Additional method development is needed to provide verification that the purity levels can be achieved for those elements.

The analyses show that Gd was at ~30% of the limit in the feed solution prior to precipitation, compared to 150 and 60% for the first and second batches of PuO₂, respectively, after calcination. The additional impurity may have resulted from using filtration equipment that was not thoroughly cleaned and recycling the filtrate to rinse precipitate out of the beaker. This potential cause is consistent with the first batch containing more Gd than the second batch, as the equipment would have been rinsed somewhat during first batch operations. Because the purity specification for Gd is quite low at 3 µg/g Pu (Column A) and Gd has been used in H Canyon dissolution campaigns, it will be important to ensure that the MOX Feed process equipment be adequately cleaned to ensure PuO₂ product batches meet specifications. In addition, a check of the purity of feed chemicals and process solutions should be considered by HB-Line to ensure sufficient product purity.

The carbon content of the two calcination batches of PuO₂ was 280 – 290 µg C/g Pu, which meets the 1000 µg C/g Pu specification. The PuO₂ samples produced in both batches had particles sizes that ranged from 0.2 – 74.0 µm, with mean particle sizes of 11.8 – 12.2 µm. These results meet the specification of < 200 µm. For the two batches, the volume percent of particles < 5.50 µm was 13.9 – 14.0 %. The specific surface areas of the PuO₂ samples were 9.22 – 9.63 m²/g.

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LIST OF ABBREVIATIONS

ANN	aluminum nitrate nonahydrate
BET	Brunauer-Emmett-Teller
BV	bed volume
DE	Destructive Evaluation
DI	deionized water
FMI	Fluid Metering Inc.
IC	ion chromatography
ICP-ES	inductively coupled plasma emission spectroscopy
ICP-MS	inductively coupled plasma mass spectroscopy
MOX	Mixed Oxide
PHA	pulse height analysis
PSA	particle size analysis
RH	relative humidity
SEM	scanning electron microscopy
SRNL	Savannah River National Laboratory
SSA	specific surface area
TGA-MS	thermogravimetric analysis-mass spectrometry

1.0 Introduction

H-Canyon and HB-Line are tasked with the production of PuO₂ from a feed of plutonium metal. The PuO₂ will provide feed material for the MOX Fuel Fabrication Facility. After dissolution of the Pu metal in H-Canyon, the solution will be transferred to HB-Line for purification by anion exchange. Subsequent unit operations include Pu(IV) oxalate precipitation, filtration and calcination to form PuO₂. This report details the results from SRNL anion exchange, precipitation, filtration, calcination, and characterization tests, as requested by HB-Line¹ and described in the task plan². This study involved an 80-g batch of Pu and employed test conditions prototypical of HB-Line conditions, wherever feasible. In addition, this study integrated lessons learned from earlier anion exchange³ and precipitation and calcination⁴ studies.

H-Area Engineering selected direct strike Pu(IV) oxalate precipitation⁵ to produce a more dense PuO₂ product than expected from Pu(III) oxalate precipitation. One benefit of the Pu(IV) approach is that it eliminates the need for reduction by ascorbic acid. The proposed HB-Line precipitation process^{1,2} involves a digestion time of 5 minutes after the time (44 min) required for oxalic acid addition. These were the conditions during HB-line production of neptunium oxide (NpO₂). In addition, a series of small Pu(IV) oxalate precipitation tests with different digestion times were conducted to better understand the effect of digestion time on particle size, filtration efficiency and other factors.⁴

To test the recommended process conditions, researchers performed two nearly-identical larger-scale precipitation and calcination tests. The calcined batches of PuO₂ were characterized for density, specific surface area (SSA), particle size, moisture content, and impurities.

Because the 3013 Standard requires that the calcination (or stabilization) process eliminate organics, characterization of PuO₂ batches monitored the presence of oxalate by thermogravimetric analysis-mass spectrometry (TGA-MS). To use the TGA-MS for carbon or oxalate content, some method development will be required. However, the TGA-MS is already used for moisture measurements. Therefore, SRNL initiated method development for the TGA-MS to allow quantification of oxalate or total carbon. That work continues at this time and is not yet ready for use in this study. However, the collected test data can be reviewed later as those analysis tools are available.

2.0 Experimental Procedure

2.1 Reagents

Reagent-grade nitric and oxalic acids were used for anion exchange and precipitation solutions. Distilled water (from the SRNL laboratory system) was used to dilute feed solutions. Deionized water (i.e., distilled water treated by Millipore Synergy 185 de-ionizer) was used for preparation of all anion exchange wash and elution acid solutions and for the oxalic acid solution used for precipitation. For dissolution of the purified PuO₂, the high-purity “Optima” grade HNO₃ and HF were used.

2.2 Plutonium Purification by Anion Exchange

2.2.1 Column Description

The ion exchange column was fabricated from 54.4-mm (inside diameter) borosilicate glass tubing (1.5-mm wall thickness) by the SRNL Glass Shop (Figure 2-1). A coarse frit was sealed into the bottom of the column to hold the resin. Graduations in “cm” were affixed to the column

(Figure 2-1). Approximately 1.47 L of Reillex™ HPQ anion exchange resin were loaded into the column for a bed height of 63.5 cm. The top of the column contained a screen that pressed and held the resin in place (Figure 2-2). This enables the column to be used with either upward or downward flow. Solutions were fed to the column using a Fluid Metering Inc. (FMI) QV-50 piston pump. Polyethylene tubing (6.35 mm outside diameter) linked feed bottles, effluent collection bottles, and the pump to the column.

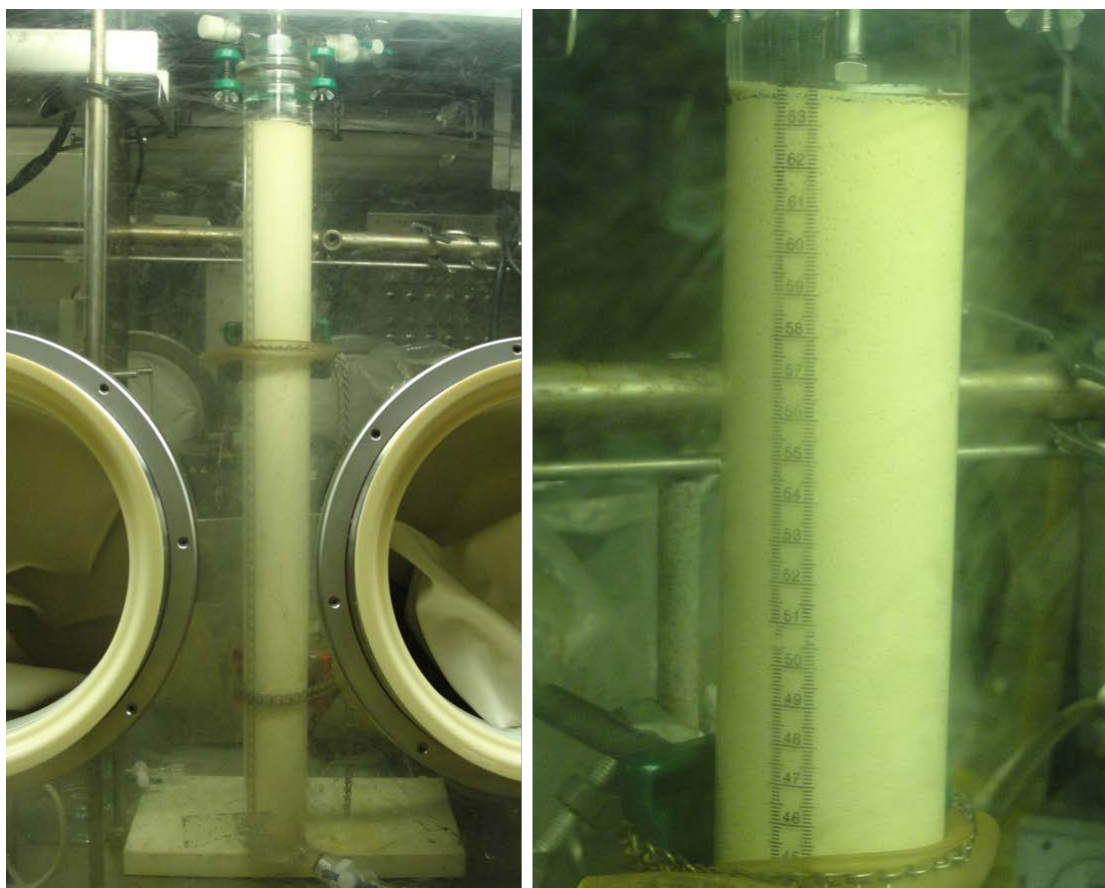


Figure 2-1. Ion Exchange Column in Glovebox

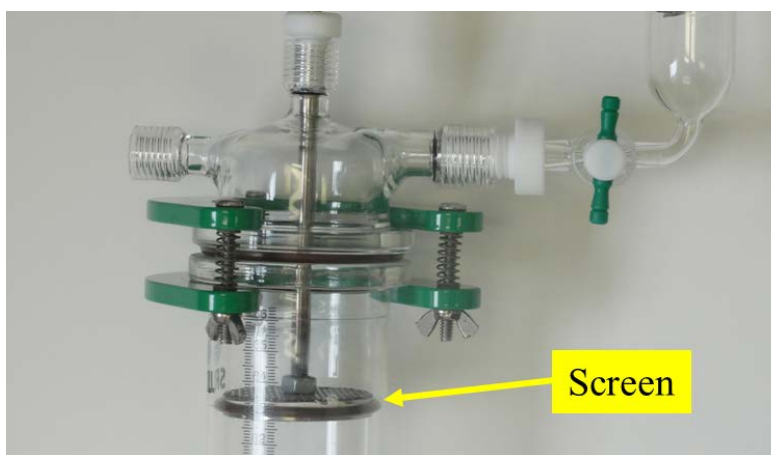


Figure 2-2. Ion Exchange Column Screen for Resin Retention

2.2.2 Plutonium Feed Solutions

Feed solutions came from four source materials. Only Feed 4 was formulated to match the expected characteristics of Pu solution from H-Canyon. Consequently, the four feed sources were not blended. Feeds 1-3 were provided to increase the amount of Pu loading on the column.

- 1) 1.0 L of legacy Pu solution from sodium peroxide fusion of 3013 Destructive Evaluation (DE) material. The total NO_3^- concentration was ~ 7.5 M and the HNO_3 concentration was ~ 6 M. The solution contained ~ 8.2 g of Pu. Due to the uncertainty associated with the solution, the solution was treated with ferrous sulfamate to convert Pu^{6+} to Pu^{3+} , heated to 50°C for 60 min to convert Pu^{3+} to Pu^{4+} , and acidified with 15.7 M HNO_3 to a final volume of 1550 mL.
- 2) 250 mL of dissolved δ -phase metal. The solution contained ~ 0.4 g of Pu. The solution concentrations were 10 M HNO_3 , ~ 0.05 M KF, and 1.5 g/L Gd. To the solution were added 12.5 mL of 2.0 M aluminum nitrate nonahydrate (ANN) solution to complex fluoride at a 2:1 Al:F molar ratio and 50 mL distilled water to reduce the total NO_3^- concentration, yielding an HNO_3 concentration of 8 M and a nitrate concentration of 8.2 M. The solution was not filtered after the addition of ANN and distilled H_2O .
- 3) 850 mL of dissolved δ -phase metal. The solution contained ~ 4.3 g of Pu. The solution concentrations were 9.3 M HNO_3 , ~ 0.044 M KF, and 0.67 g/L Gd. To the solution were added 40 mL of 2.0 M ANN solution to complex fluoride at a 2:1 Al:F molar ratio and 60 mL distilled water to reduce the total NO_3^- concentration, yielding an HNO_3 concentration of 8.3 M and a nitrate concentration of 8.6 M. The solution was not filtered after the addition of ANN and distilled H_2O .
- 4) 14.9 L of dissolved 3013 DE materials from several sources. The material was dissolved using sodium peroxide fusion. Consequently, the solution was high in sodium (Na). The solution contained ~ 75 g of Pu. The total NO_3^- concentration was ~ 8.3 M and the HNO_3 concentration was ~ 7.9 M. The solution was filtered through a 5-micron filter. In addition, the following chemicals were added to the solution on a per-liter basis.
 - Gallium (Ga): 2 wt % of the Pu feed (~ 5 g/L) was added as gallium nitrate [0.374 g].
 - Boron (B): 1.2 g/L was added as boric acid [6.86 g].
 - Potassium fluoride (KF): 0.08 M was added as KF [4.65 g].
 - Aluminum (Al): 2 mol of Al per mol of fluoride added as aluminum nitrate nonahydrate (ANN) [60.0 g].
 - Chloride: 5 mg chloride per gram of Pu added as sodium chloride (NaCl) [0.041 g].
 - Iron and packaging can: 0.23 g per gram of Pu added as packaging can [1.16 g].
 - Nylon bag: 0.0093 g per gram of Pu added as nylon sleeve [0.046 g].

2.2.3 Column Operation

The ion exchange resin was conditioned with downward flow, loaded and washed with upward flow, and eluted with downward flow. Although HB-Line conditions in the upward flow direction, the difference in operation for conditioning will not affect the test results.

Prior to loading Pu onto the resin, the column was conditioned with 3 L of 8 M HNO_3 at ~ 90 mL/min. Plutonium feed solutions were fed to the column at an average rate of 87 mL/min (maximum of 118 mL/min and minimum of 71 mL/min). Feed solutions 1-3 listed above were combined and fed to the column first. Afterward, the 14.9 L of primary feed (Feed 4 listed above) was fed to the column. After the loading of each bottle, the height of Pu in the column was recorded. Samples of the composite effluent solutions were submitted for analyses. The effluent from Feeds 1-3 was analyzed as Load Eff 1. The first 4000 mL of Item 4 effluent were

analyzed as Load Eff 2. The next 6000 mL of Feed 4 effluent were analyzed as Load Eff 3. The final 4900 mL of Item 4 effluent were analyzed as Load Eff 4.

The column was then washed with 15 L of 8 M HNO₃ to remove non-Pu impurities. The first liter of wash was loaded at 77 mL/min. Subsequent wash solutions were fed to the column at an average rate of 175 mL/min (maximum of 182 mL/min and minimum of 167 mL/min). After the loading of each bottle, the height of Pu in the column was recorded. Each composite bottle of wash solution was sampled and analyzed.

After washing was complete, the pump speed was reduced to 56 mL/min and the Pu on the column was eluted with 0.35 M HNO₃. The effluent was collected in a graduated bottle. When the volume in the collection bottle was 450 mL, 600 mL, 750 mL, and 900 mL, grab samples of the effluent solution were collected directly from the column (referred to as Heads 0.3, 0.4, 0.5 and 0.6, respectively). At 1000 mL, Pu was observed eluting from the column and the effluent was directed to a separate graduated collection bottle to collect the Hearts cut. This first 1000 mL of composite effluent was labeled and analyzed as Heads. Grab samples were collected of the Hearts Product effluent when the total volume reached 1050 mL and 1200 mL (referred to as Heads 0.7 and 0.8, respectively, although these samples were collected from the Hearts cut).

When the volume of effluent in the Hearts cut reached 1460 mL, 1600 mL, and 1760 mL, samples of the effluent were collected (referred to as Hearts 60, 55, and 50, respectively). At 1760 mL in the Hearts cut, the effluent was directed to a separate graduated bottle labeled as Tails 1. Samples of the effluent were collected when the total effluent volume (from the beginning of the Hearts cut) reached 1950 mL, 2200 mL, and 2500 mL (referred to as Hearts 45, 40, and 35, respectively, although these samples were actually collected from the Tails cut). A sample of the Tails 1 composite bottle was also collected for analysis.

At this time, the effluent was directed to a bottle labeled as Tails 2, and the pump rate was increased to ~120 mL/min. Approximately 1900 mL of 0.35 M HNO₃ was fed through the column and collected in the Tails 2 bottle. A sample of the Tails 2 composite bottle was collected for analysis. Pictures of the column 1) after loading, 2) during washing, and 3) during elution are shown in Figure 2-3.

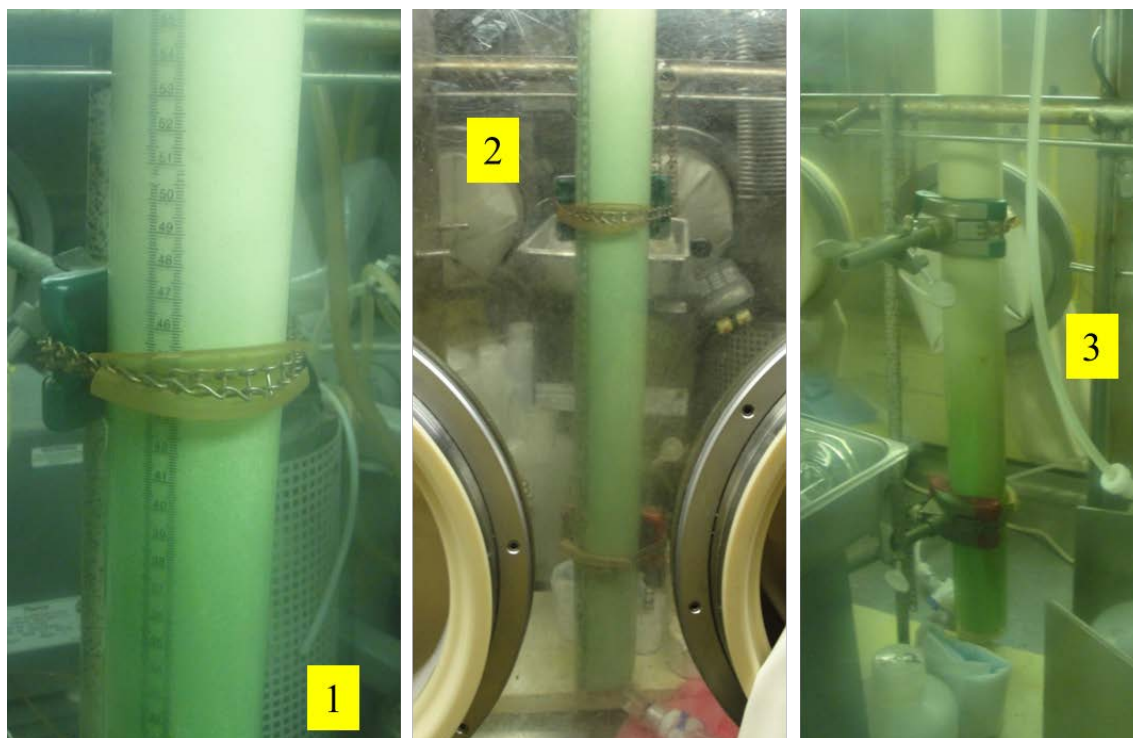


Figure 2-3. Ion Exchange Resin 1) after Loading, 2) during Washing, and 3) during Elution

2.2.4 Characterization

A list of samples collected and analyses conducted is provided in Table 2-1. The samples with volume of 2 mL are grab samples. Note that after analysis of the Product solution, the acidity of the Product was increased by addition of 7.0 M HNO₃. The resulting Adjusted Product solution was analyzed and used for precipitation. Samples for inductively coupled plasma-emission spectroscopy (ICP-ES) were submitted in plastic sample vials; all other samples were submitted in glass sample vials.

The feed, product and other effluent solutions from the anion exchange column experiment were characterized by some or all of these methods: gamma pulse height analysis (PHA), inductively coupled plasma-mass spectroscopy (ICP-MS), ICP-ES, ion chromatography (IC) for anions, and free acid. To achieve lower detection limits and reduce interferences for some impurities in the Pu product solution, the Pu product solution was analyzed by ICP-MS and ICP-ES after Pu removal. The details of that method development effort are reported elsewhere.⁶

2.3 Precipitation

The Pu product solution described above was sampled and then re-sampled a week later after thorough mixing. After receiving the acid analysis of the well-mixed solution, a researcher added 7.0 M HNO₃ to raise the Pu solution to a target concentration of ~1.5 M HNO₃. The researcher then mixed the Adjusted Product solution, sampled it, and initiated the first precipitation with approximately half of the Pu solution. The next day, the researcher performed the second precipitation with the remaining solution. No valence adjustments were performed before either of the precipitation steps. Prior to each precipitation batch, researchers calculated the volume of 0.9 M oxalic acid needed to achieve 0.1 M excess oxalic acid after Pu precipitation. That volume of 0.9 M oxalic acid was transferred into a 250-mL bottle. For each precipitation, purified Pu solution was heated in a stainless steel beaker to 50 ± 2 °C. Researchers used a 2-L stainless steel

beaker for both batches (nominally 40 g Pu each). Once the Pu solution reached nominally 50 °C, 0.9 M oxalic acid was added at a flow rate of 12.5 mL/min to target a total oxalic acid addition time of 44 minutes, which corresponds to expected HB-Line precipitation conditions.⁵ A summary of the precipitation conditions is provided in the Results section.

Table 2-1. List of Samples Submitted for Analyses

Sample ID	Volume (mL)	AD #	Analyses*
Feed Item 1	1550	300299075	1, 3, 4
Feed Item 4	14900	300299076	1, 3, 4
Load Eff 1	2250	300299083	1, 2
Load Eff 2	4000	300299084	1, 2
Load Eff 3	6000	300299085	1, 2
Raffinate of Primary Feed	2	300299322	3,4,5
Load Eff 4	4600	300299086	1, 2
Wash 1	1000	300299089	1, 3, 4
Wash 2	2000	300299090	1, 3, 4
Wash 3	2000	300299091	1, 3, 4
Wash 4	2000	300299092	1, 3, 4
Wash 5	2000	300299093	1, 3, 4
Wash 6	2000	300299094	1, 3, 4
Wash 7	2000	300299095	1, 3, 4
Wash 8	2000	300299096	1, 3, 4
Heads 0.3	2	300299097	1
Heads 0.4	2	300299098	1
Heads 0.5	2	300299099	1
Heads 0.6	2	300299100	1
Heads 0.7	2	300299101	1
Heads 0.8	2	300299102	1
Heads	1000	300299103	1
Product	1760	300299294	1, 3, 4, 5, 6,7
Adjusted Product	1890	300299638	1, 6
Hearts 60	2	300299077	1
Hearts 55	2	300299078	1
Hearts 50	2	300299079	1
Hearts 45	2	300299080	1
Hearts 40	2	300299081	1
Hearts 35	2	300299082	1
Tails 1	1000	300299087	1
Tails 2	1900	300299088	1
* Analytical methods below with typical uncertainties. 1 = gamma spectroscopy, ± 5% 2 = Pu TTA, ± 5% 3 = inductively coupled plasma mass spectroscopy (ICP-MS), ± 20% 4 = inductively coupled plasma emission spectroscopy (ICP-ES), ± 10% 5 = ion chromatography (IC), ± 10% 6 = total acid / free acid, ± 10% 7 = Additional ICP-MS and ICP-ES analysis after Pu removal			

For both 40-g precipitation batches, the digestion time, or time between the end of oxalic acid addition and the start of filtration, was 5 minutes. Following each precipitation, the Pu oxalate slurry was poured into a stainless steel filter housing containing a nominally 10- μm stainless steel filter screen material provided by HB-Line. The bulk of the Pu oxalate slurry was transferred to the filter housing and the liquid was vacuum filtered and collected in a 1-L filter flask. Then, the filter apparatus was moved to a second 1-L filter flask. Filtration continued and the filtrate recovered in the first flask was used to rinse the slurry out of the stainless steel beaker until essentially all Pu oxalate solids were in the filter housing.

During filtration, cake washing (with 1.4 M HNO_3 /0.1 M oxalic acid) did not occur nor was cake wash solution added to the precipitator vessel, as is done in HB-Line to assist in flushing the solids out of the precipitator. Thus, this study was conservative in the sense that the use of some cake wash solution, as done in HB-Line, would likely improve the purity of the final PuO_2 product because the cake wash or flush solution dilutes the impurities held up in the filter cake.

For Demo 1, the vacuum continued to operate for 10 minutes after standing liquid was gone from the cake. The cake was left open overnight and vacuum was again applied for 40-50 minutes the next day. Then Demo 1 cake was transferred to a tared quartz crucible and weighed. The crucible containing the Demo 1 oxalate cake was left on the balance and additional mass measurements were recorded to gauge drying.

The stainless steel beaker used during precipitation was cleaned with 1.4 M HNO_3 /0.1 M oxalic acid and rinsed three times with distilled water prior to the second (Demo 2) precipitation. After the Demo 2 precipitation and filtration, vacuum filtration continued for approximately 15 minutes after no liquid was visible on top of the cake. The cake was exposed to air overnight. Filtrate solutions were characterized by gamma PHA to determine Pu losses to the filtrate. Filtrate solutions were also characterized by ICP-MS, ICP-ES and IC. Samples of $\text{Pu}(\text{C}_2\text{O}_4)_2$ from both Demo 1 and 2 were evaluated for Particle Size Analysis (PSA) in a solution of 1.4 M HNO_3 /0.1 M oxalic acid.

2.4 Calcination

Calcinations were performed in a nominal 110-mL quartz crucible. Each crucible had a Pu-oxalate bed depth of approximately 2-3 cm. As noted in previous SRNL work⁷ with neptunium oxide (NpO_2) calcinations, we assumed that a bed depth of 2-3 cm (or less for later in this study) would allow enough air to permeate the powder during calcination that the PuO_2 produced would be similar to that produced in HB-Line at similar conditions. This assumption seems reasonable because in the case of NpO_2 , the batches of NpO_2 calcined at SRNL at 600 and 650 °C for 2 hours had specific surface areas which bounded that of the NpO_2 made by HB-Line early in the production campaign as shown in Table 2-2.⁸ The HB-Line design, which passes air through the filter cake (or powder bed) during calcination, effectively removes moisture and oxalate decomposition products from the filter cake. The design may have other advantages for the properties of the PuO_2 .

Table 2-2. BET Specific Surface Area for NpO_2

NpO_2 Material	BET Specific Surface Area, m^2/g
SRNL 600 °C	5.34
SRNL 650 °C	3.67
HB-Line	4.03

The target calcination conditions for the study were 40-44 g Pu in each batch, calcined at 650 °C for four hours. For the first batch, the actual calcination time extended to 4.5 h due to an unexpected laboratory safety condition. Following each calcination, the resulting PuO₂ was cooled briefly and transferred to a glass jar, which was placed inside two zippered plastic bags.

2.5 Plutonium Oxide Characterization

The PuO₂ sample from the Demo 1 batch was characterized by thermogravimetric analysis-mass spectrometry (TGA-MS) for moisture content, which included initial duplicate analysis as well as analyses after exposure to humid air. Measurements were made using a Netzsch 409 PC Luxx[®] TGA and a Pfeiffer ThermoStar[™] MS. An argon purge stream passed through the TGA sample chamber, then through a tube heated to 180 °C, to a sample point where the MS continuously samples the TGA off-gas. The TGA-MS was calibrated for moisture using gypsum (CaSO₄•2H₂O) standards. This study used a calibrated Vaisala HM34F temperature and humidity meter for measuring glovebox conditions during Demo 1 analyses and exposures; however, Demo 2 analyses were delayed due to TGA instrument issues.

Samples of PuO₂ from both Demo 1 and Demo 2 were characterized by (1) the Brunauer-Emmett-Teller (BET) method for SSA using a Micromeritics 2365 Gemini surface area analyzer, (2) PSA using a Microtrac X100 Particle Size Analyzer with a 250-mL recirculator and a distilled water matrix, (3) Scanning Electron Microscopy (SEM), (4) bulk and tapped density, pycnometry density, carbon/sulfur analysis, and (5) dissolution in 12 M HNO₃/0.1 M HF followed by analysis by gamma PHA, ICP-MS and ICP-ES.

Note that the dissolution of purified PuO₂ samples in 12 M HNO₃/0.1 M HF occurred in virgin polypropylene vessels within a hot block at 95 °C for 3 h. After the 3-h dissolution, personnel detected no visible solids in the solutions. Samples of the dissolved PuO₂ were analyzed directly as well as after removal of Pu to enable lower detection limits. For these dissolved PuO₂ samples, several measures were taken to reduce the levels of contaminants introduced by the Pu removal method described earlier, which was used for the anion exchange product solution.⁶ The nitric acid used in the improved process was spectroscopy grade (Optima) stocks as opposed to ACS grade (reagent) stocks. The use of sodium nitrite was eliminated from the process, as it was expected that the bulk of the plutonium was already in the tetravalent state. Finally, the first 20 vol % of the sample load solution was used as a rinse to purify the resin bed. The first 20 vol % aliquot that flowed through the resin beds was discarded. The remaining 80 vol % of the sample load solution was then purified by contacting it through the rinsed resin beds prior to submitting for further analyses by ICP-MS.

For the ICP-ES analysis of purified, dissolved PuO₂, the same improvements were used – higher purity acid and use of the first 20 vol % of the solution to rinse the resin. For these ICP-ES solutions, however, resin beds of 2.2-mL cartridge volumes of TEVA[®] were used to extract tetravalent plutonium from the sample solutions.

3.0 Results and Discussion

3.1 Plutonium Purification by Anion Exchange

Analysis of the hearts cut by ICP-MS measured 45.6 g/L for Masses 239-241 and a ²³⁹Pu enrichment of 94%. Gamma spectroscopy analysis measured 42.1 g/L ²³⁹Pu. Factoring for the enrichment measured by ICP-MS, the total Pu concentration determined using gamma spectroscopy was 44.8 g/L. Free acid analysis measured 1.23 M H⁺. Ion chromatography measurement reported fluoride < 10 mg/L, chloride < 10 mg/L and nitrate = 1.77 M. In this case,

the analyses confirm one another. The gamma analysis of 44.8 g Pu/L converts to 0.19 M Pu. It is expected that the Pu is present as Pu(IV), which is associated with four nitrate ions per Pu ion, yielding 0.75 M nitrate complexing the Pu. Combining the free acid (nitric acid) result of 1.23 M with the 0.75 M nitrate complexing the Pu yields an expected total nitrate of 1.98 M. The ion chromatography analysis of total nitrate is within 12% of this prediction.

Analytical results from the anion exchange column experiment are provided in Appendix A, and generally confirm expectations concerning resin performance. A plot of the Pu and ²⁴¹Am content of the solution exiting the resin column is shown in Figure 3-1, using average feed concentrations of 4.7 g Pu/L and 0.3 g Am/L for comparison. Because the Pu concentration was below the detection limit for gamma spectroscopy for the first six wash bottles, the data from ICP-MS were plotted. Thus, the slight increase in Pu concentration observed as loading ended and washing began may have been due in part to switching from gamma to ICP-MS values, as ICP-MS values are reported at ±20%. During both loading and wash cycles, the Pu concentration exiting the column increases, which is expected due to the limited amount of open sites on the resin for Pu sorption. Loading of the Primary Feed proceeded at nominally 17 mg Pu/min/cm², using the average flow rate. Then, after the first liter (0.68 BV) of wash, the volumetric flow rate increased by a factor of two for the remaining 9.52 BV of wash. In Figure 3-1, elution begins at 21.9 BVs and the Hearts cut occurs from 22.5 to 23.7 BVs.

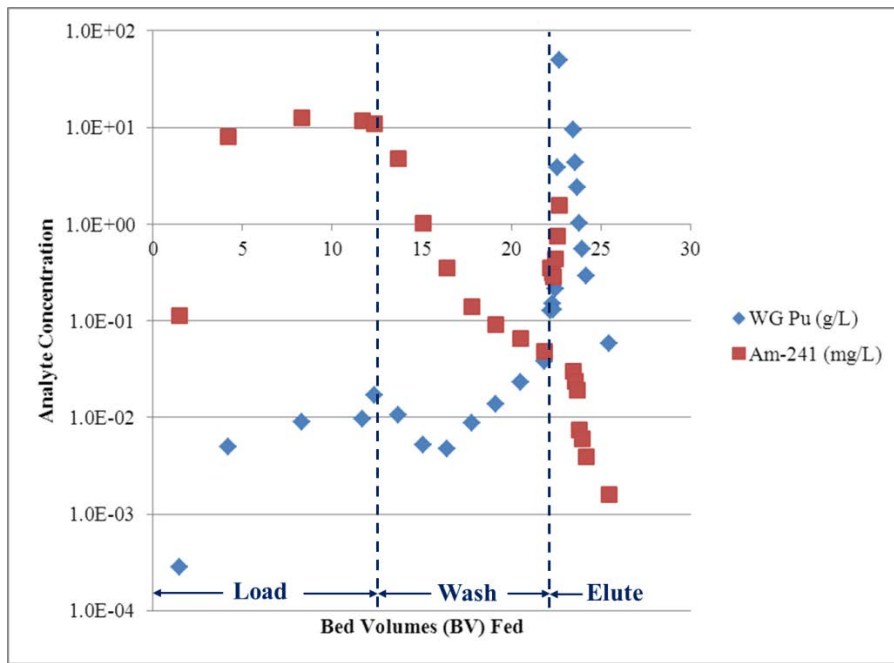


Figure 3-1. Pu and ²⁴¹Am Released from Resin Column

The elution profile for the column experiment is provided in Figure 3-2. The Heads cut begins at 0 BV. The Hearts cut begins at 0.68 BV and ends at 1.80 BV. Figure 3-2 shows that a minor amount of entrapped ²⁴¹Am releases as the Pu elutes. This behavior is similar to what has been observed with boron and gadolinium.³

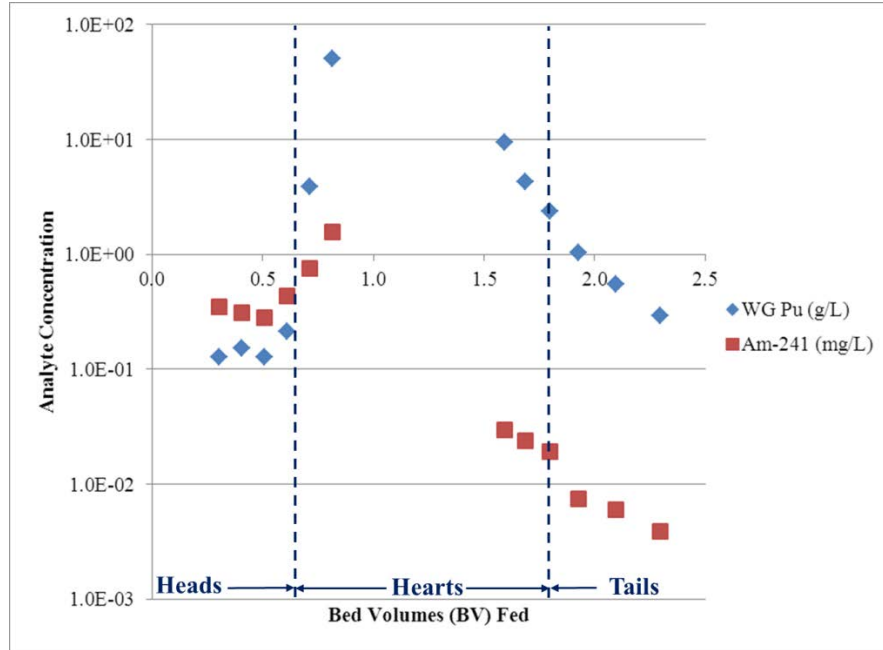


Figure 3-2. Pu and ²⁴¹Am Elution Profile

This experiment included ~10 BV of wash, and the Pu product solution was relatively pure, as shown in Table 3-1 and 3-2. Also shown in these tables are the concentration profiles of the various elements during column washing with 8 M HNO₃.

Table 3-1. Sample Analyses by ICP-ES

Element	Feed Item 1 (mg/L)	Feed Item 4 (mg/L)	Wash 1 (mg/L)	Wash 2 (mg/L)	Wash 3 (mg/L)	Wash 4 (mg/L)	Wash 5 (mg/L)	Wash 6 (mg/L)	Wash 7 (mg/L)	Wash 8 (mg/L)	Product (mg/L)
Al	44.6	4320	3760	262	4.08	1.65	1.47	0.703	< 0.599	< 0.599	< 5.99
B	< 5.7	1110	1030	94.1	1.95	0.864	0.635	0.411	0.209	0.217	< 5.7
Ba	1.49	1.83	1.43	0.215	0.101	0.272	5.06	0.238	0.108	< 0.097	< 1.1
Be	5.1	1.93	1.7	0.119	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.08
Ca	37.9	44.7	34.9	3.07	0.382	0.307	1.07	0.338	0.156	0.262	< 7
Cd	< 1.21	< 1.21	< 0.121	< 0.121	< 0.121	< 0.121	< 0.121	< 0.121	< 0.121	< 0.121	< 3.6
Ce	< 7.91	< 7.91	6.26	6.24	4.8	3.81	2.43	1.96	1.28	0.815	< 12.4
Co	< 1.83	< 1.83	0.548	< 0.183	< 0.183	< 0.183	< 0.183	< 0.183	< 0.183	< 0.183	< 1.83
Cr	74.2	42.2	35.3	2.55	0.077	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 2.16
Cu	8.6	9.41	7.01	0.621	< 0.186	< 0.186	< 0.186	< 0.186	< 0.186	< 0.186	< 8.52
Fe	4630	1210	1050	82.3	1.81	1.06	0.844	1.3	0.252	0.381	< 3.94
Gd	< 3.84	< 3.84	< 1.92	< 0.192	< 0.192	< 0.192	< 0.192	< 0.192	< 0.192	< 0.192	< 1.92
K	2950	1810	1600	125	< 3.4	< 3.4	< 3.4	< 3.4	< 3.4	< 3.4	< 76.4
Mg	121	40.1	33.3	2.39	0.167	0.122	1.28	0.192	0.028	0.053	< 0.11
Mn	25.3	7.1	5.6	0.435	< 0.034	< 0.034	< 0.034	< 0.034	< 0.034	< 0.034	< 3.4
Mo	< 16.4	< 16.4	3.67	< 1.12	< 1.12	< 1.12	< 1.12	< 1.12	< 1.12	< 1.12	< 16.4
Na	24500	14300	11200	782	14.1	5.63	8.84	2.44	0.977	1.07	< 23
Ni	79.3	95.4	78	5.58	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< 3.7
Pb	< 17.6	< 17.6	6.18	< 1.76	< 1.76	< 1.76	< 1.76	< 1.76	< 1.76	< 1.76	< 17.6
S	6690	< 300	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Si	70.7	< 21.5	5.46	1.9	0.897	0.902	0.852	0.991	2.29	1.56	< 21.5
Sn	<14.7	<14.7	5.23	< 1.47	< 1.47	< 1.47	< 1.47	< 1.47	< 1.47	< 1.47	< 29.4
Sr	<0.2	<0.2	0.167	0.017	< 0.015	< 0.015	0.121	< 0.015	< 0.015	< 0.015	< 0.1
Ti	1.59	1.29	1.32	0.085	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.4
Zn	3.6	3.56	2.22	0.444	0.313	0.356	20.9	2.15	0.15	0.232	< 1.31
Zr	192	< 0.63	0.587	0.109	< 0.056	< 0.056	< 0.056	< 0.056	< 0.056	< 0.056	< 1.26

Note: highlighted cells indicate values below the method detection limit.

Results in Tables 3-1 and 3-2 are for solutions without Pu removal. Later in this report, analyses of the Product solution after removal of Pu are reported and evaluated. Analytical and operating data from the anion exchange column test, such as radioactive dose rates which are largely due to ²⁴¹Am, are included in Appendix Tables A-1 and A-2. In addition, in Appendix Tables A-3 and A-4, results for Feed Item 4, the Primary Feed, are shown next to results of the Primary Feed Raffinate sample, which is essentially the Primary Feed after removal of Pu by the anion exchange column. The results show very good agreement between the two analyses.

Table 3-2. Sample Analyses by ICP-MS

Mass Number	Feed Item 1 (mg/L)	Feed Item 4 (mg/L)	Wash 1 (mg/L)	Wash 2 (mg/L)	Wash 3 (mg/L)	Wash 4 (mg/L)	Wash 5 (mg/L)	Wash 6 (mg/L)	Wash 7 (mg/L)	Wash 8 (mg/L)	Product (mg/L)
59	1.15	0.774	0.575	0.047	< 0.020	< 0.020	0.023	< 0.020	< 0.020	< 0.020	< 0.020
63	3.01	6.16	4.35	0.356	< 0.095	< 0.095	< 0.095	< 0.095	< 0.095	< 0.095	< 0.095
65	0.980	2.74	1.88	0.053	< 0.035	< 0.035	< 0.035	< 0.035	< 0.035	< 0.035	< 0.035
69	45.5	61.5	55.9	3.53	0.052	0.030	0.039	< 0.025	< 0.025	< 0.025	< 0.025
71	31.4	43.9	36.9	2.40	0.035	0.022	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
88	0.304	0.209	0.298	0.067	0.061	0.058	0.191	0.068	0.051	0.062	< 0.020
89	0.513	0.622	0.455	0.042	< 0.015	< 0.015	0.051	< 0.015	< 0.015	< 0.015	< 0.015
90	131	0.661	0.384	0.085	0.026	0.033	0.025	0.033	< 0.020	0.029	< 0.02
91	26.6	0.163	0.101	0.022	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
92	44.2	0.955	0.626	0.126	0.018	0.017	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
94	46.2	0.654	0.414	0.084	0.016	< 0.015	< 0.015	0.015	< 0.015	< 0.015	< 0.015
95	0.671	0.752	0.600	0.092	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
96	8.22	0.780	0.614	0.093	0.016	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
97	0.374	0.445	0.340	0.052	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
98	1.04	1.08	0.836	0.149	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
100	0.414	0.478	0.335	0.057	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
106	0.813	< 0.200	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
107	0.275	< 0.050	< 0.025	0.029	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	0.070
108	0.288	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
110	0.379	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
112	0.140	0.085	0.076	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
114	0.127	0.105	0.053	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
116	0.310	0.880	0.800	0.068	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
117	0.181	0.429	0.398	0.043	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
118	0.483	1.45	1.315	0.142	0.038	< 0.023	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
119	1.37	1.03	0.444	0.042	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	1.43
120	20.4	10.9	1.66	0.141	0.018	0.019	0.024	0.038	0.054	0.083	122
121	0.275	0.103	0.087	0.036	0.014	0.012	< 0.010	< 0.010	< 0.010	< 0.010	0.218
122	0.135	0.357	0.344	0.031	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
123	0.194	< 0.100	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045	< 0.045
124	0.209	0.564	0.523	0.042	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
135	0.077	0.099	0.086	0.011	< 0.010	< 0.010	0.048	< 0.010	< 0.010	< 0.010	< 0.010
137	0.104	0.227	0.160	0.018	< 0.010	< 0.010	0.084	< 0.010	< 0.010	< 0.010	< 0.010
138	0.671	1.253	0.913	0.116	0.029	0.032	0.561	0.033	< 0.020	< 0.020	< 0.020

Note: highlighted cells indicate values below the method detection limit

Table 3-2. Sample Analyses by ICP-MS (cont'd)

Mass Number	Feed Item 1 (mg/L)	Feed Item 4 (mg/L)	Wash 1 (mg/L)	Wash 2 (mg/L)	Wash 3 (mg/L)	Wash 4 (mg/L)	Wash 5 (mg/L)	Wash 6 (mg/L)	Wash 7 (mg/L)	Wash 8 (mg/L)	Product (mg/L)
140	1.25	5.83	5.45	5.16	3.76	2.87	2.08	1.60	1.14	0.648	5.44
142	0.179	0.777	0.700	0.628	0.459	0.371	0.280	0.194	0.143	0.074	0.735
144	< 0.050	0.08	< 0.010	< 0.010	< 0.010	< 0.010	0.017	< 0.010	< 0.010	< 0.010	< 0.010
146	< 0.050	0.05	< 0.010	< 0.010	< 0.010	< 0.010	0.013	< 0.010	< 0.010	< 0.010	< 0.010
155	0.113	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
156	0.170	0.099	0.087	0.075	0.058	0.036	0.039	0.023	0.023	0.011	0.122
157	0.128	< 0.050	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
158	0.203	< 0.050	0.017	0.014	0.015	0.011	0.013	0.011	< 0.010	< 0.010	< 0.010
160	0.163	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
166	0.370	< 0.050	0.034	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
167	0.238	< 0.050	0.019	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
168	0.264	< 0.050	0.023	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
170	0.150	< 0.050	0.016	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
176	0.070	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
177	0.240	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
178	0.349	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
179	0.177	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
180	0.473	< 0.050	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
181	3.91	0.162	0.166	0.093	0.126	0.036	0.130	0.072	0.018	< 0.010	< 0.010
182	6.25	0.851	0.654	0.151	0.045	0.032	0.022	0.020	0.016	0.016	0.092
183	3.28	0.434	0.383	0.094	0.028	0.018	0.014	0.011	0.012	0.011	< 0.010
184	6.92	1.05	0.762	0.181	0.048	0.037	0.029	0.029	0.022	0.032	0.104
186	6.81	0.922	0.684	0.167	0.046	0.032	0.031	0.024	0.021	< 0.015	0.109
206	0.254	0.861	0.829	0.196	0.017	< 0.010	0.011	< 0.010	< 0.010	< 0.010	< 0.010
207	0.245	0.809	0.731	0.166	0.013	< 0.010	0.011	< 0.010	< 0.010	< 0.010	< 0.010
208	0.581	2.05	1.71	0.388	0.038	< 0.015	0.021	0.026	< 0.015	< 0.015	< 0.015
234	0.639	0.166	0.212	0.208	0.143	0.081	0.051	0.042	0.019	0.012	0.070
235	30.8	6.04	7.98	8.30	5.06	3.00	1.89	1.12	0.649	0.313	1.54
236	2.46	1.22	1.53	1.59	0.994	0.630	0.362	0.213	0.120	0.062	0.336
237	1.06	0.621	0.126	0.128	0.092	0.07	0.04	0.04	0.03	0.03	5.58
238	4.07	1.68	0.937	0.955	0.656	0.375	0.248	0.142	0.083	0.041	5.38
239	7400	4416	6.44	5.90	3.95	4.13	8.12	13.0	18.2	25.9	42900
240	483	283	0.392	0.367	0.234	0.260	0.48	0.79	1.09	1.57	2640
241	23.5	15.0	10.1	4.29	0.979	0.286	0.136	0.096	0.082	0.051	34.4

Note: highlighted cells indicate values below the method detection limit

3.2 Precipitation

Analysis of the well-mixed anion exchange Pu product solution showed 1.23 M free acid and 44.8 g Pu/L. To increase the acidity to ~1.5 M, 100 mL of 7.0 M HNO₃ were added to the remaining 1.75 L of Pu product solution. Analysis of the Adjusted Product solution showed 1.54 M free acid and 44.1 g Pu/L. The Adjusted Product analysis yielded a total Pu mass (including samples) of 87.3 g Pu, which was 4% higher than the total Pu based on the non-adjusted Product, but within the reported uncertainty of 5.0% for gamma PHA analyses. Summaries of the precipitation conditions and results are shown in Table 3-3. and 3-4 Based on the Adjusted Product analyses, the excess oxalic acid for the Demo 1 precipitation batch was 0.09 M, and that of the Demo 2 batch was 0.10 M, both within the proposed HB-Line operating range of 0.10 ± 0.01 M excess oxalic acid.

Table 3-3. Precipitation Conditions

Batch	44.1 g/L Pu mL	0.9 M Oxalic mL	Oxalic acid addition time, min	Digestion Time min	Wash Solution mL	Vacuum Drying Time min
Demo 1	944	540	43	5	0	50-60
Demo 2	895	525	42	5	0	15

Table 3-4. Precipitation Results

Batch	Pu in Feed g	Pu Oxalate g	Pu in Filtrate [†] g	% Pu Losses to Filtrate
Demo 1	41.6	107.815	0.14	0.34
Demo 2	39.4	103.602	0.16	0.41

[†] Determined by gamma PHA with isotopic ratio by ICP-MS.

3.3 Calcination

Using a calcination temperature of 650 °C, the $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ samples were converted to PuO_2 . For the two calcinations, Appendix A (Figures A-1 and A-2) provides furnace and sample temperature profiles. Table 3-5 shows the masses of the initial oxalate material prior to calcination and the mass of the resulting PuO_2 product, along with the theoretical dry amounts. Taking an average of the two batches, the actual Pu-oxalate mass was about 50% higher than the theoretical dry Pu-oxalate mass. This result indicates that about one-third of the $\text{Pu}(\text{C}_2\text{O}_4)_2$ cake was water, including molecularly-bound waters of hydration and loosely-bound moisture.

Table 3-5. Mass Changes during Calcination

Batch	Pu in Feed g	Dry Pu Oxalate (Theory) g	Pu Oxalate (Actual) g	PuO_2 (Theory) g	PuO_2 (Actual) g [†]
Demo 1	41.6	72.2	107.815	47.2	46.2
Demo 2	39.4	68.4	103.602	44.7	43.7

[†] These values reflect total product recovered, not including SEM samples.

After calcination for the specified time, the quartz crucible was removed from the furnace at temperature and cooled briefly before the sample was transferred to a jar. Exposure times are provided in Table 3-6, along with ambient glovebox conditions. The jar was covered with a lid and placed into a secondary plastic bottle with a lid to minimize exposure to humid air.

Table 3-6. Glovebox Conditions after Calcination

Calcination Batch	Before or After Calcination	Glovebox Conditions		Time for Cooling and Transfer into Jar
		T °C	RH %	min
Demo 1	Before	23.7	55.7	15
	After	NM	NM	
Demo 2	Before	19.2	64.1	18
	After	23.7	48.8	

NM = not measured

Photographs of the Pu oxalate in a quartz crucible prior to calcination and the PuO₂ after calcination are shown in Figure 3-3. Though the photographs are from different batches, the Demo 2 batch contained nearly the same amount of Pu as Demo 1. Thus, Figure 3-3 depicts the volume (and color) change that occurs during calcination. The left portion of Figure 3-3 also shows the two thermocouples used for measuring cake temperature.

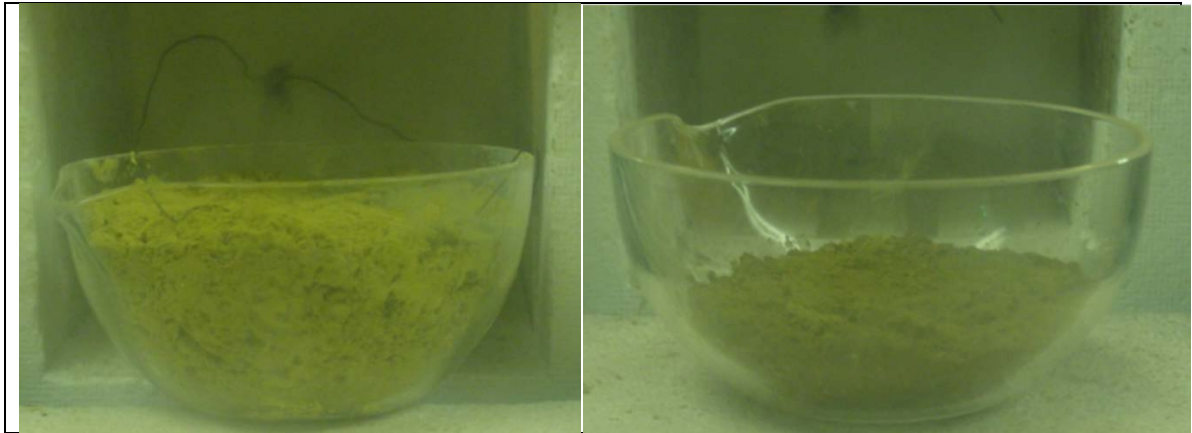


Figure 3-3. Left: Demo 1 Pu Oxalate; Right: Demo 2 PuO₂ after Calcination.

Samples of PuO₂ from both batches were submitted for morphology characterization by SEM, as shown in Figure 3-4, Figure 3-5, and Figure 3-6.

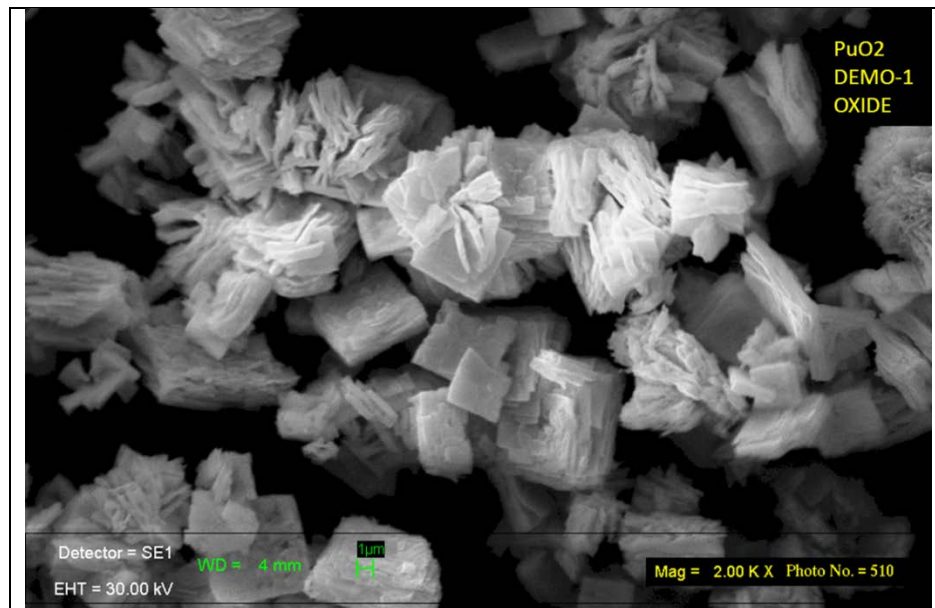


Figure 3-4. Typical SEM Results for Demo 1 PuO₂

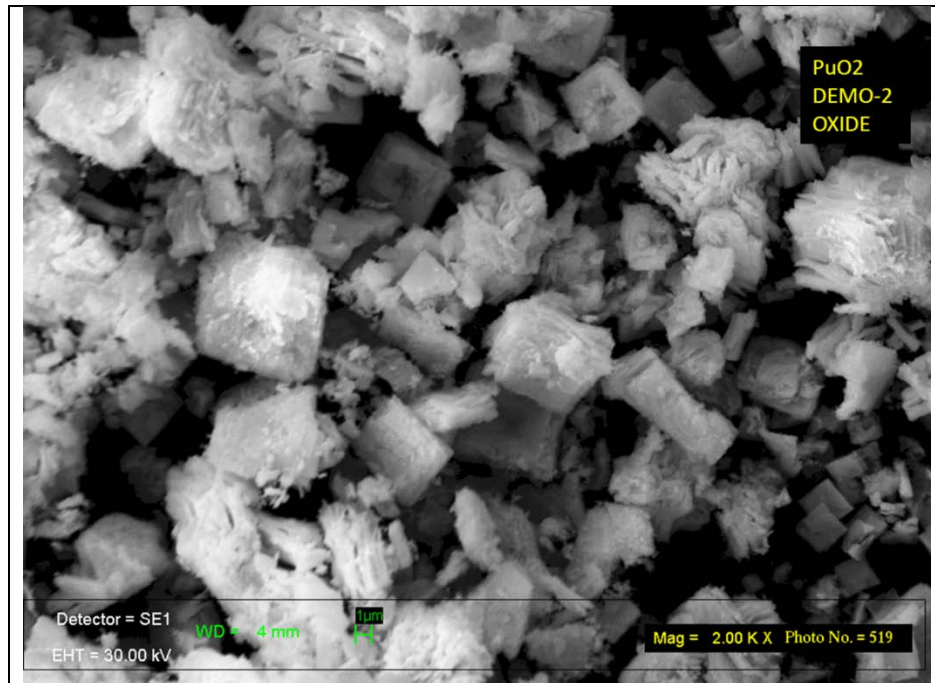


Figure 3-5. SEM Results for Demo 2 PuO₂, Showing Some Irregular Particles

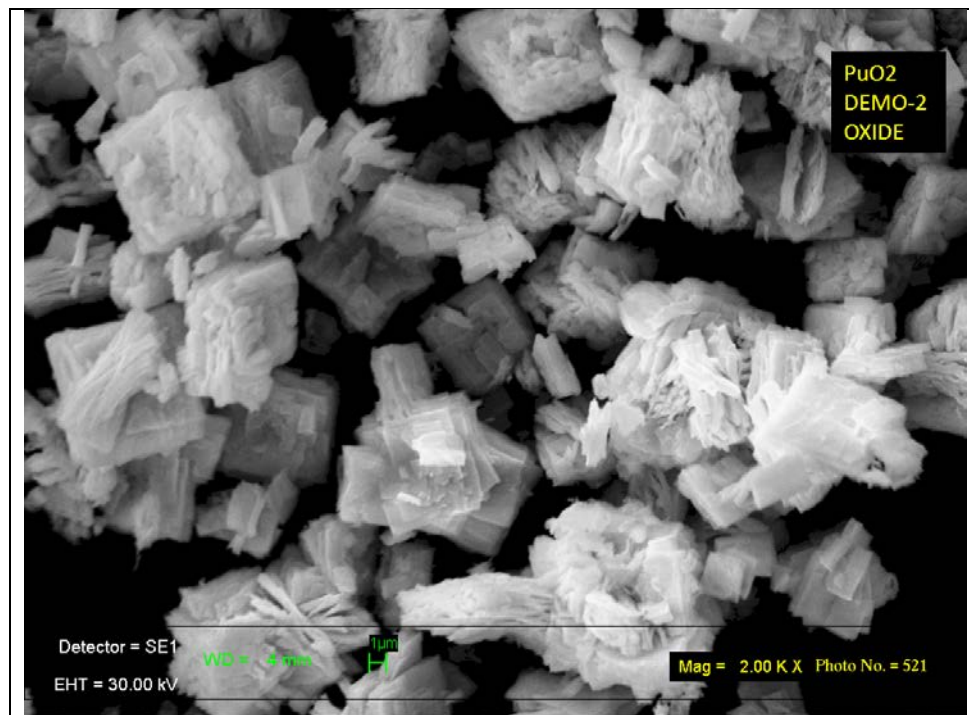


Figure 3-6. SEM Results for Demo 2 PuO₂, Showing Typical Particles

3.3.1 Moisture Analysis by TGA-MS

Typical TGA-MS plots for PuO₂ samples produced in this study are shown in Figure 3-7, Figure 3-8, and Figure 3-9.

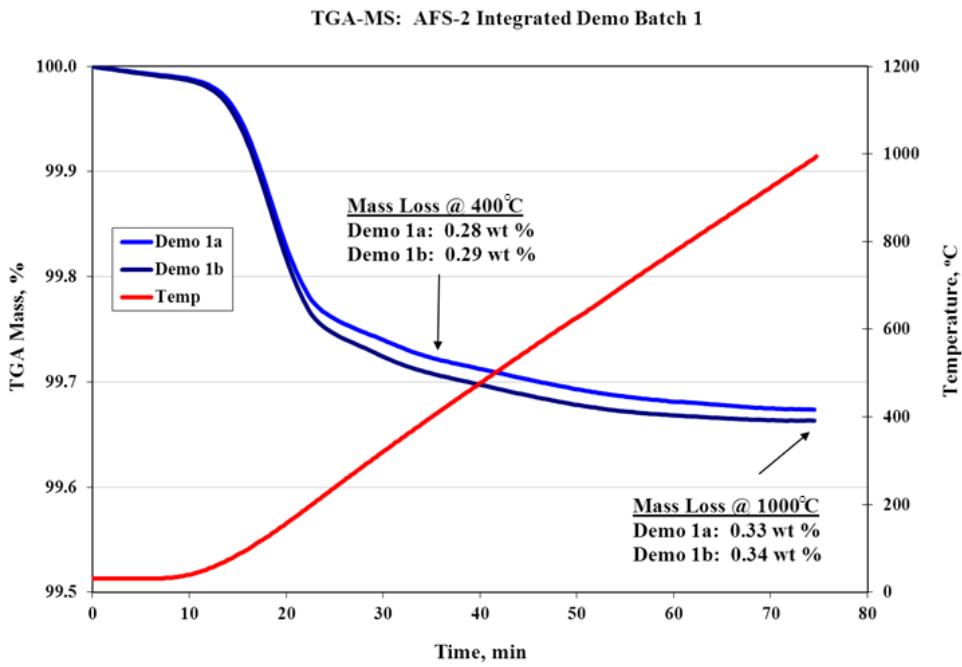


Figure 3-7. TGA Mass Measurements for Demo 1a and Demo 1b Samples

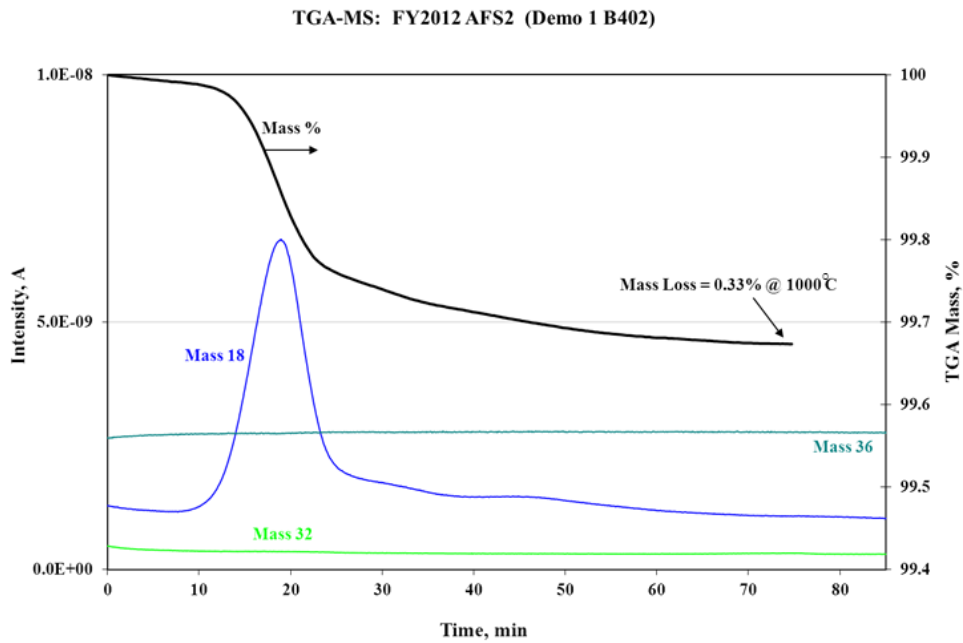


Figure 3-8. MS Signals (linear scale) from TGA-MS Analysis of Demo 1a Sample

TGA-MS: FY2012 AFS2 (Demo 1 B402)

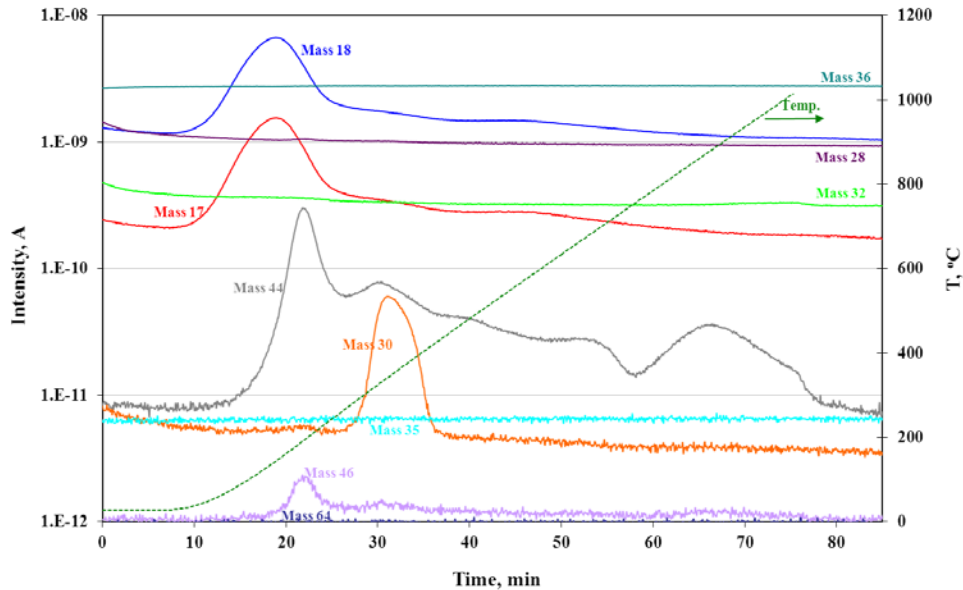


Figure 3-9. MS Signals (logarithmic scale) from TGA-MS Analysis of Demo 1a Sample

As shown in the figures, heating to 400 °C caused release of nearly all of the moisture from both samples Demo 1a and 1b. In addition, the largest portion of the carbon release, measured as Mass 44 or CO₂, occurred in the same ~40-300 °C temperature range as the bulk of the moisture release (Figure 3-8 and Figure 3-9). With carbon dioxide, however, its release continued through heating, with a second, smaller release centered at ~850 °C. A release of Mass 30, attributed to NO, occurred in the 300 – 500 °C range. The TGA-MS showed no other significant gas releases, including no Mass 28 (attributed to CO). Approximately 90% of the total mass loss for each sample was associated with water loss. Quantitative TGA-MS results are shown in Table 3-7. .

Table 3-7. TGA-MS Results for Integrated Demonstration “Demo 1” Sample

Sample	Total TGA mass loss wt %	MS Moisture wt %
Demo 1a	0.33	0.30
Demo 1b	0.34	0.32
After analysis of Demo 1a and 1b, all of remaining sample was exposed to air at 44-60% RH for at least 4 days.		
Demo 1c [†]	> 0.48 (~0.6)	> 0.42
Demo 1d, Argon, Room Temp. for 1 h	0.30	0.26
Demo 1e, Argon, ~50 °C for 1 h	0.36	0.37
Demo 1f, Argon, ~93 °C for 1 h	0.45	0.44
The 95% Confidence Intervals for MS moisture contents are ±10% or slightly better and are provided in Appendix Table A-5.		

[†]TGA test ended at ~240 °C.

After exposing the Demo 1 sample to humid air at 44-60% RH for four days, analyses began on portions of the exposed sample. Unfortunately, during analysis of the first exposed sample portion, Demo 1c, the TGA sample thermocouple failed. Based on the standard temperature profile and time, the TGA heated the sample to only ~240 °C. The results for Demo 1c are shown in Figure 3-10. Comparing these Demo 1c results to those of Demo 1a and 1b indicates that the 0.42 wt % moisture observed for the Demo 1c sample amounted to approximately 70% of the moisture in sample Demo 1c. Extrapolating the data, the extended, non-prototypical exposure to humid air likely caused the Demo 1 material to reach ~0.6 wt %, which exceeds the acceptable moisture limit of 0.50 wt %. Small amounts of CO₂ were also observed, but its mass was negligible compared to that of water.

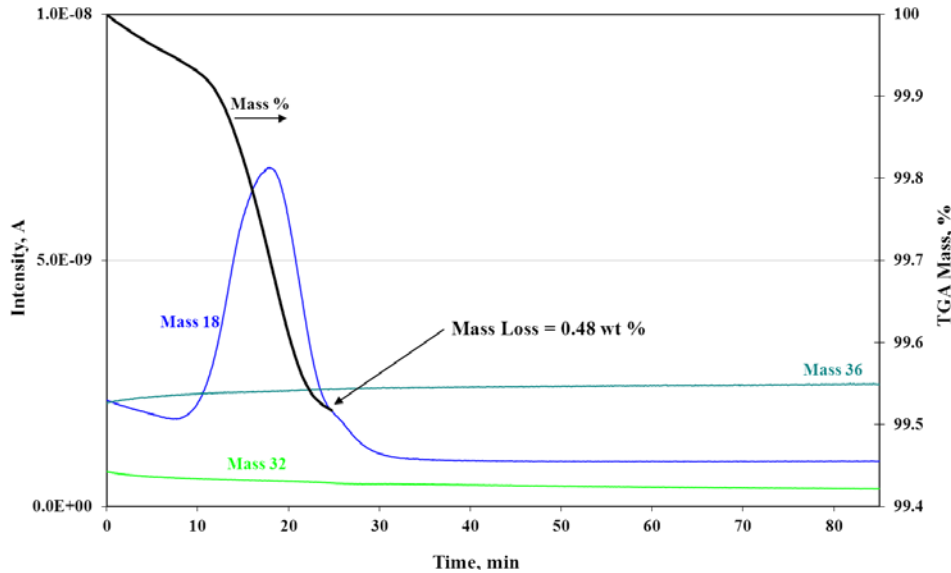


Figure 3-10. TGA-MS for Demo 1c Sample

To gauge the effectiveness of an inert purge gas for drying the moist Demo 1 material, sample portions were placed inside the argon purge stream of the TGA. One portion was kept at room temperature for 1 h, while the other two portions were heated to either ~50 °C or ~93 °C and held at temperature for 1 h. For the sample kept at room temperature in flowing argon, the sample lost 0.30 wt %, as shown in Figure 3-11, and likely would have continued to lose mass with additional time.

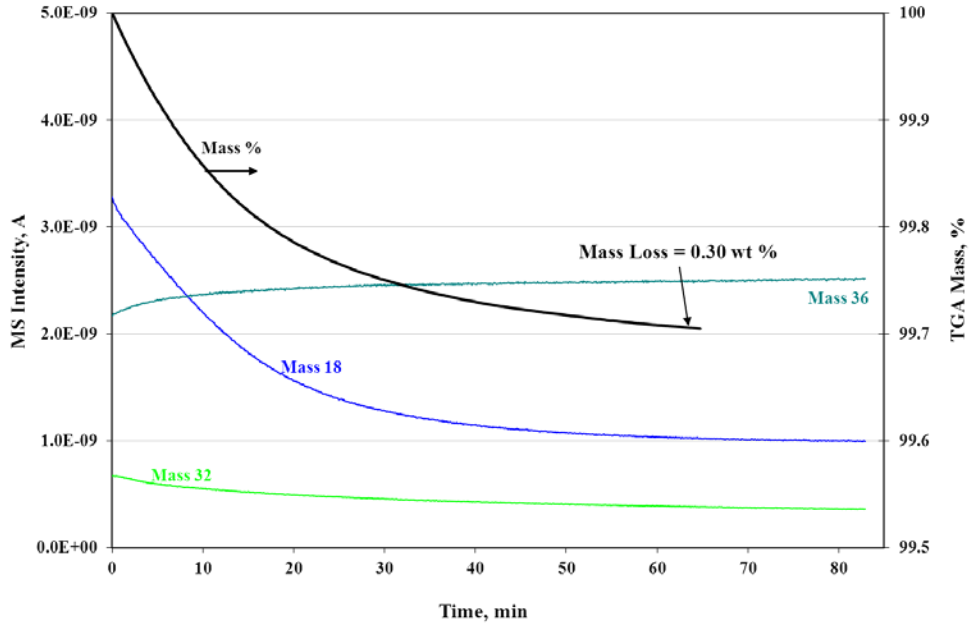


Figure 3-11. TGA-MS for Demo 1 Sample in Dry Argon at Room Temperature for 1 h.

Similarly, as shown in Figure 3-12 and Figure 3-13, the Demo 1 sample portions heated to 50 and 93 °C lost a significant amount of moisture in the first 30 minutes and continued to lose moisture at a slower rate thereafter. The TGA mass losses of 0.36 and 0.45 wt % were essentially all due to moisture, based on the measured MS moisture contents of 0.37 and 0.44 wt %, respectively, for the Demo 1 samples at 50 and 93 °C. Assuming an estimated starting moisture content of ~0.6 wt %, the use of dry argon would be sufficient to achieve the required moisture content of <0.50 wt %. These results suggest that future work is warranted if a need exists to dry similar PuO₂ materials using an inert gas.

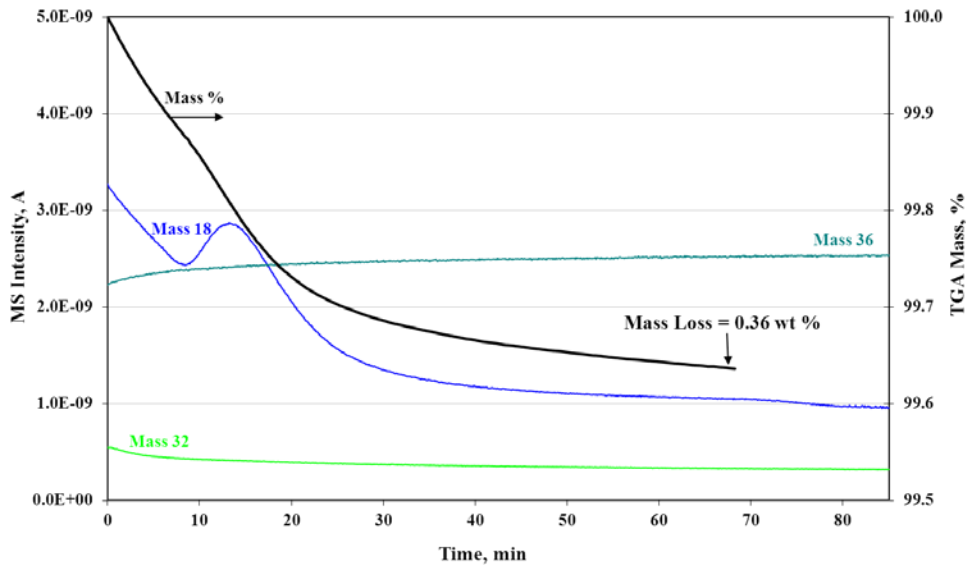


Figure 3-12. TGA-MS for Demo 1 Sample in Dry Argon at ~50 °C for 1 h.

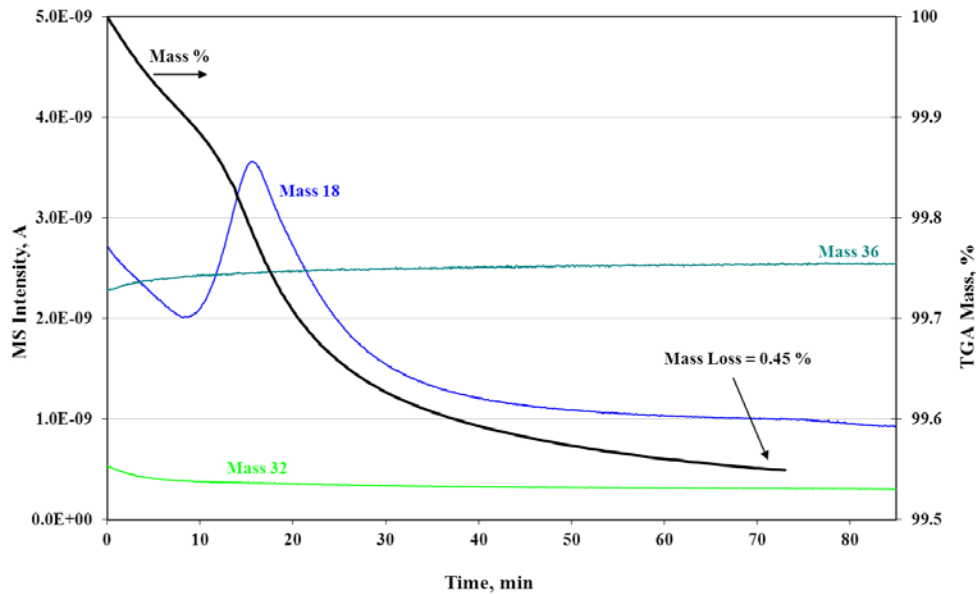


Figure 3-13. TGA-MS for Demo 1 Sample in Dry Argon at ~93 °C for 1 h.

3.3.2 Specific Surface Area

The SSA for samples from the two demonstration batches are shown in Table 3-8.

Table 3-8. Specific Surface Area Measurements and Uncertainties

Sample	SSA m ² /g	95% Confidence Interval	
		Lower Bound	Upper Bound
Demo 1	9.63	9.45	9.80
Demo 2	9.22	9.14	9.30

Generally, SSA samples are analyzed in duplicate and the average is reported. The expected SSA range⁹ for calcination at 650 °C is 5-14 m²/g. The confidence interval for a specific sample depends in part on the precision of the duplicate portions of that sample. For this study, the SSA 95% confidence intervals correspond to uncertainties ranging from ± 0.87% to ± 1.87 %.

3.3.3 Carbon and Sulfur Analysis

Results for carbon and sulfur content for the samples analyzed are shown in Table 3-9. Future plans include comparing carbon analysis by TGA-MS to these values measured by a carbon analyzer. The values in Table 3-9 show that the carbon content of PuO₂ produced at SRNL easily met the Column A limit of 1000 µg C/g Pu and the Column B limit of 500 µg C/g Pu. For these samples, carbon analyses were performed in triplicate, and the standard deviation of the replicates was less than 20%. The sulfur content of PuO₂ produced at SRNL also easily met the Column A and B limits of 250 µg S/g Pu.

Table 3-9. Carbon and Sulfur Contents of PuO₂ Samples

Batch	C wt%	C µg/g sample	C µg/g Pu [†]	Uncertainty
Demo 1	0.025	250	290	± 20%
Demo 2	0.021	240	280	± 20%
	S wt%	S µg/g sample	S µg/g Pu [†]	Uncertainty
Demo 1	< 4E-6	< 0.040	< 0.046	± 10%
Demo 2	< 4E-6	< 0.040	< 0.046	± 10%

[†] Based on estimated assay of 0.87 g Pu/g PuO₂ sample.

3.3.4 Particle Size Analysis

Personnel performed PSA on both PuO₂ and Pu oxalate samples. The MOX specification¹⁰ states that the maximum particle size shall be 200 µm with as few sub-5-µm as practical. The test results are summarized in Table 3-10, and the plots of particle size distribution are provided in the Appendix (Figures A-3 through A-6). The data in Table 3-10 indicate that the products meet the specification.

Table 3-10. Particle Size Analyses of Pu Oxalate and PuO₂ Samples

Sample ID	Particle Size Range µm	Mean* Particle Size µm	Volume % of Particles < 5.50µm
Demo 1 PuO ₂	0.204 – 74.0	12.2	14.0
Demo 2 PuO ₂	0.204 – 74.0	11.8	13.9
Demo 1 Pu Oxalate	0.344 – 124.5	13.2	16.8
Demo 2 Pu Oxalate	0.409 – 124.5	17.1	10.3

*Mean Particle Size determined on a volumetric basis.

3.3.5 Density

The bulk and tapped densities for the Demo 1 and 2 samples are shown in Table 3-11. For each measurement, the full sample was used. Hence, after the “Demo 1A” analysis, the full sample was poured back into the sample vial. The sample was then poured again into the graduated cylinder for a second (“Demo 1B”) measurement of bulk and tapped densities. The bulk density is measured after the powder is poured into a graduated cylinder. The tapped density is measured after the graduated cylinder has been lightly tapped for five minutes.

The pycnometry density of both samples was also measured, as shown in Table 3-11. Pycnometry is a measure of the density of the material excluding the void space between particles. To measure pycnometry accurately, samples larger than the 7-13 g samples used in this study are recommended. Though the small sample sizes add some uncertainty to the pycnometry results, it is notable that the pycnometry densities agree with the published PuO₂ density of 11.46 g/cm³.¹¹

Table 3-11. Density Measurements

	Bulk Density g/cm³	Powder Tap Density g/cm³	Material Density by Pycnometry g/cm³
Demo 1A	1.57	2.05	11.73
Demo 1B	1.53	2.11	
Demo 2A	1.53	2.06	11.07
Demo 2B	1.56	2.07	

3.3.6 Analysis of Dissolved PuO₂

The gamma PHA results for the four dissolved 0.25 g portions of PuO₂ (two portions from each Demo batch) showed dissolved Pu contents of nominally 8-9 g Pu/L. To compare the impurity contents of these samples to the Column A Limits², the analysis results are color-coded in Table 3-12. Red indicates the limit was not attained. For all of the “red” analytes except Gd (K, Mo, P, and Si), the solutions showed less than the detection limit, but the limits were above the Column A specification. It should be noted that C and S were measured using the carbon-sulfur analyzer discussed in Section 3.3.3; ²⁴¹Am was determined by gamma analysis. All other results in Table 3-12 were determined by ICP-ES or ICP-MS, as indicated.

For analytes in which the Column A limit was attained, the closeness to the limit is indicated, in order, by the colors yellow, white, and green. Yellow indicates an impurity concentration between 50% and 100% of specification. White indicates an impurity concentration between 10% and 50% of specification. Green indicates an impurity concentration below 10% of specification. Elements measured by ICP-MS have been corrected assuming naturally-occurring isotopic abundance.

Table 3-12. Impurity Contents of Dissolved PuO₂ Solution

Element	Isotope Used by ICP-MS	Column A Limit $\mu\text{g/g Pu}$	Demo 1 $\mu\text{g/g Pu}$	Demo 2 $\mu\text{g/g Pu}$	% of Column A Limit (Average)
Ag	--	250	< 134.3	< 141.8	< 55.2
Al	--	500	165.1	< 79.2	24.4
²⁴¹ Am (gamma)	--	7000	24.1	27.0	0.4
B	--	100	< 71.4	< 75.4	< 73.4
Be	--	100	< 1.0	< 1.1	< 1.0
C (LECO)	--	1000	290	280	28.5
Ca	--	500	207.5	27.7	23.5
Cd (ICP-MS)	¹¹¹ Cd	10	< 0.44	< 0.46	< 4.6
Cd (ICP-MS)	¹¹³ Cd	10	< 4.62	< 4.87	< 47.4
Co	--	100	< 22.9	< 24.2	< 23.5
Co (ICP-MS)	⁵⁹ Co	100	< 0.34	< 0.36	< 0.35
Cr	--	1000	< 27.1	< 28.6	< 2.8
Cu	--	100	< 23.4	< 24.7	< 24.0
Dy (ICP-MS)	¹⁶³ Dy	1	1.25	0.46	85.2
Eu (ICP-MS)	¹⁵¹ Eu	1	< 0.15	< 0.16	< 15.2
Eu (ICP-MS)	¹⁵³ Eu	1	0.16	< 0.14	< 15.3
Fe	--	2000	< 144.5	< 86.3	5.8
Ga	--	12000	< 24.0	< 25.4	< 0.2
Ga (ICP-MS)	⁶⁹ Ga	12000	< 0.75	< 0.79	< 0.006
Ga (ICP-MS)	⁷¹ Ga	12000	< 0.21	< 0.22	< 0.002
Gd (ICP-MS)	¹⁵⁵ Gd	3	4.25	1.79	101
Gd (ICP-MS)	¹⁵⁷ Gd	3	4.94	1.83	113
K	--	300	< 426.5	< 450.5	< 146.2
Li	--	400	< 21.6	< 22.8	< 5.5
Mg	--	500	< 12.4	< 13.1	< 2.6
Mn	--	100	< 4.3	< 4.5	< 4.4
Mo	--	100	< 139.9	< 147.8	< 143.8
Na	--	1000	197.2	101.5	14.9
Ni	--	5000	< 46.4	< 49.0	< 1.0
P	--	200	< 515.7	< 544.6	< 265.1
Pb (ICP-MS)	²⁰⁶ Pb	200	< 23.4	< 24.7	< 12.0
Pb (ICP-MS)	²⁰⁷ Pb	200	< 25.5	< 26.9	< 13.1
Pb (ICP-MS)	²⁰⁸ Pb	200	< 21.5	< 22.7	< 11.1
S (LECO)	--	250	< 0.046	< 0.046	< 0.02
Si	--	200	< 2408.7	< 1661.8	< 1017.6
Sm (ICP-MS)	¹⁴⁷ Sm	2	0.93	< 0.50	< 35.8
Sm (ICP-MS)	¹⁴⁹ Sm	2	0.72	< 0.54	< 31.5
Sn (ICP-MS)	¹¹⁸ Sn	100	< 18.6	< 19.6	< 19.1
Sn (ICP-MS)	¹²⁰ Sn	100	< 17.4	< 18.4	< 17.9
Ta (ICP-MS)	¹⁸¹ Ta	200	13.3	15.4	7.2
Th (ICP-MS)	²³² Th	100	< 6.2	< 6.6	< 6.4
Ti	--	100	8.1	< 5.3	6.7
U	--	5000	< 732.3	< 773.4	< 15.1
V	--	300	< 6.5	< 6.9	< 2.2
W (ICP-MS)	¹⁸² W	200	< 15.0	< 15.9	< 7.7
Zn	--	150	20.9	< 17.4	12.8
Zr	--	50	< 7.0	< 7.4	< 14.4

For comparison, data for the starting hearts-cut solution are provided in Table 3-13. All results were determined by ICP-ES or ICP-MS, as indicated, after removal of Pu.

Table 3-13. Impurity Contents of Starting Hearts-Cut Pu Solution

Element	Isotope Used by ICP-MS	Column A Limit	Sample	Sample	% of Column A Limit (Average)
		µg/g Pu	mg/L	µg/g Pu	
Ag	--	250	< 5.35	< 119.4	< 47.8
Al	--	500	< 3	< 67.0	< 13.4
B	--	100	< 2.85	< 63.6	< 63.6
Be	--	100	< 0.04	< 0.9	< 0.9
Ca	--	500	< 7.97	< 177.9	< 35.6
Cd (ICP-MS)	¹¹³ Cd	10	< 0.0095	< 1.74	< 17.4
Co	--	100	< 0.915	< 20.4	< 20.4
Co (ICP-MS)	⁵⁹ Co	100	< 0.00062	< 0.014	< 0.01
Cr	--	1000	< 0.54	< 12.1	< 1.2
Cu	--	100	< 0.93	< 20.8	< 20.8
Dy (ICP-MS)	¹⁶³ Dy	1	< 0.00062	< 0.056	< 5.6
Eu (ICP-MS)	¹⁵³ Eu	1	< 0.00062	< 0.0265	< 2.7
Fe	--	2000	4.78	106.7	5.3
Ga (ICP-MS)	⁶⁹ Ga	12000	0.0066	0.245	0.002
Gd (ICP-MS)	¹⁵⁵ Gd	3	0.0058	0.875	29.2
Gd (ICP-MS)	¹⁵⁷ Gd	3	0.0076	1.09	36.2
K	--	300	< 38.2	< 852.7	< 284
Li	--	400	< 0.86	< 19.2	< 4.8
Mg	--	500	< 9.4	< 209.8	< 42.0
Mn	--	100	< 0.17	< 3.79	< 3.8
Mo	--	100	< 5.58	< 124.6	< 125
Na	--	1000	< 25.5	< 569.2	< 56.9
Ni	--	5000	< 1.85	< 41.3	< 0.8
P	--	200	< 27.3	< 609.4	< 305
Pb (ICP-MS)	²⁰⁶ Pb	200	< 0.031	< 2.87	< 1.4
Pb (ICP-MS)	²⁰⁷ Pb	200	< 0.031	< 3.13	< 1.6
Si	--	200	< 10.8	< 241.1	< 121
Sm (ICP-MS)	¹⁴⁷ Sm	2	< 0.00062	< 0.092	< 4.6
Sm (ICP-MS)	¹⁴⁹ Sm	2	< 0.00062	< 0.100	< 5.0
Sn (ICP-MS)	¹¹⁸ Sn	100	0.0087	0.799	0.8
Sn (ICP-MS)	¹²⁰ Sn	100	0.031	2.14	2.1
Ti	--	100	< 0.2	< 4.46	< 4.5
U	--	5000	< 29.2	< 651.8	< 13.0
V	--	300	< 0.26	< 5.80	< 1.9
Zn	--	150	< 0.655	< 14.6	9.7
Zr	--	50	< 0.28	< 6.25	< 12.5

In Table 3-12 there are five elements that may exceed the Column A limit –Gd, K, Mo, P, and Si. Of these, four of the analyte (K, Mo, P, and Si) measurements are below the method detection limit. Therefore, only Gd was positively detected above the Column A limit. Of the five elements that exceed the Column A limit in Table 3-12, four of them are also above the limit in Table 3-13. However, in all four cases, the concentrations in Table 3-13 are below the measurement detection limit.

Table 3-13 shows that Gd was at ~30% of the Column A limit in the feed prior to precipitation, compared to 153% and 60% for the first and second batches, respectively, after calcination. The source of the additional impurity is not clear. However, in this study the filtrate solutions were recycled and used to rinse the precipitate out of the beaker. This method differed from the method used in the smaller-scale study completed recently on the same equipment. It is likely that the filtrate collection beakers were not thoroughly cleaned and rinsed, and that recycling of the filtrate, therefore, introduced contamination into the Pu oxalate, which was retained during calcination. Analyses of nitric and oxalic acids used in this study did not show detectable Gd. However, the challenging specifications for several elements make it important to ensure that feed chemicals used by HB-Line are sufficiently pure. For the reagent grade nitric and oxalic acids used in this study, analytical results are provided in the Appendix, and show that the reagents used in this study did not contribute significant impurities to the Pu solution and the PuO₂ powder produced.

Of the four elements that exceed the Column A limit in both tables, none of them are expected to be retained by the anion exchange column, nor are they expected to precipitate with oxalic acid. Kyser and King previously reported on the behavior of K, Mo, P, and Si in anion exchange and their expected level in the feed materials.³ Consequently, based on process knowledge and the absence of data positively confirming that K, Mo, P, and Si are above the Column A limit, it is expected that they are below the limit. Additional method development is needed to provide verification that the purity levels can be achieved for those elements.

4.0 Conclusions

An anion exchange column experiment produced 1.76 L of a purified 44.8 g/L Pu solution at 1.23 M free acid. After increasing the acidity to 1.54 M, researchers performed two batches of Pu(IV) oxalate precipitation at 50 °C using precipitation times expected in HB-Line. The resulting two batches of Pu oxalate were calcined separately at 650 °C for nominally four hours, with a flow of air passing through the furnace.

Replicate samples of PuO₂ from the Demo 1 batch, which had limited exposure to humid air, showed TGA mass losses of 0.33-0.34 wt % when heated to 1000 °C. Mass spectrometry evaluation of these samples indicated moisture contents of 0.30 – 0.32 wt %. Exposing additional sample Demo 1 material to humid air (44 – 60% RH) for four days yielded material that likely contained > 0.50 wt % moisture, but an instrument problem prevented heating of that sample above ~250 °C.

Subsequent studies with Demo 1 sample portions exposed to humid air showed that placing the PuO₂ in a stream of dry argon gas for 1 hour caused release of significant amounts of moisture, with a moisture loss of 0.26 wt % at room temperature, increasing to a moisture loss of 0.44 wt % at ~93 °C. Assuming an estimated starting moisture content of ~0.6 wt %, the use of dry argon would be sufficient to achieve the required moisture content of <0.50 wt %.

TGA-MS data for the Demo 1 sample was consistent with an earlier study of small-scale samples produced via similar conditions, where the bulk of the moisture was released from samples by 300 °C, along with a significant portion of the CO₂. As with earlier samples, the Demo 1 material released a minor amount of NO in the ~40-300 °C range, but did not release CO or SO₂.

Both batches of PuO₂ produced in this study exhibited good purity. In the oxide product there were five elements that may exceed the Column A limit for MOX oxide feed – Gd, K, Mo, P, and Si. Of these, four of the analyte (K, Mo, P, and Si) measurements were below the method detection limit. Therefore, only Gd was positively detected above the Column A limit. Of the five elements that exceeded the limit in the oxide product, four of them (K, Mo, P, and Si) are also above the limit in the Pu feed solution to precipitation. However, in all four cases, the concentrations in the Pu feed solution were also below the measurement detection limit.

The analyses show that Gd was at ~30% of the limit in the feed solution prior to precipitation, compared to 150 and 60% for the first and second batches of PuO₂, respectively, after calcination. The additional impurity may have resulted from using filtration equipment that was not thoroughly cleaned and recycling the filtrate to rinse precipitate out of the beaker. This potential cause is consistent with the first batch containing more Gd than the second batch, as the equipment would have been rinsed somewhat during first batch operations.

Of the four elements (K, Mo, P, and Si) that exceed the oxide product limit while being below the method detection limits, none of them are expected to be retained by the anion exchange column, nor are they expected to precipitate with oxalic acid. Consequently, based on process knowledge and the absence of data positively confirming that K, Mo, P, and Si were above the Column A limit, it is likely that they were below the limit. Additional method development should be performed to verify that the purity levels can be achieved for those elements.

The carbon content of the two calcination batches was 280-290 µg C/g Pu, which meets the 1000 µg C/g Pu specification. The PuO₂ samples produced in both batches had particles sizes that ranged from 0.2 – 74.0 µm. These results meet the specification of < 200 µm. For the two batches, the volume percent of particles < 5.50 µm was 13.9 – 14.0 %. The SSA of the PuO₂ samples was 9.22 – 9.63 m²/g. The expected SSA range was 5 – 14 m²/g.

5.0 Recommendations

To determine the operating conditions needed to dry large (kg) quantities of PuO₂ using a dry gas purge, SRNL recommends further studies. Moisture absorption studies with PuO₂ having surface areas in the region of interest, 5-14 m²/g, are recommended at the 1-40 g scale. In addition, kg-scale studies using cerium oxide (CeO₂) or a similar surrogate for PuO₂ are recommended to understand the flow rates, times, and equipment dimensions needed to dry bulk quantities of PuO₂.

To ensure sufficient purity of the H Area PuO₂ product, particularly for Gd, which is used in H Area processes, SRNL recommends consideration of reducing the presence of Gd and other impurities in tank heels, process piping, and other potential sources of impurities. Similarly, SRNL recommends consideration of the purity of feed chemicals and process solutions to ensure sufficient PuO₂ purity.

6.0 Future Work

To reduce the detection limit for boron (B) analysis, method development work at F/H Laboratory is planned. After method development progresses, the PuO₂ samples generated in this study will be analyzed for B. In addition, work is planned to determine the decontamination factor (DF) for B due to the precipitation, filtration and calcination processes. The approach for determining B DF due to the precipitation, filtration and calcination processes will likely be similar to the work done to determine the DF for fluoride and chloride ions due to the precipitation, filtration and calcination processes.¹² A sample of the PuO₂ produced in this study has been delivered to F/H Laboratory for this future work.

7.0 References

- ¹ Christopher, J.W., Task Technical Request, “Flow Sheet Verification for HB-Line Phase II Plutonium Oxide Production PPT/FLT/Calcination Operations and 3013 Equivalency”, NMMD-HTS-2011-3178, November 22, 2011.
- ² Crowder, M.L., and J.M. Duffey, “Task Technical and Quality Assurance Plan for Precipitation and Calcination of Plutonium(IV) Oxalate to Form Plutonium Oxide and Subsequent Gas Generation Studies to Support the MOX Feed Mission”, SRNL-RP-2011-01657, Rev. 0, Savannah River National Laboratory, January 15, 2011.
- ³ Kyser, E.A., and W.D. King, “HB-Line Anion Exchange Purification of AFS-2 Plutonium for MOX”, SRNL-STI-2012-00233, Savannah River National Laboratory, April 2012.
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Appendix A

Table A-1. Sample Analyses by Gamma Spectroscopy and Pu TTA.

Sample ID	²³⁹ Pu (dpm/mL)	WG Pu (g/L)	²⁴¹ Am (dpm/mL)	²⁴¹ Am (mg/L)
Feed Item 1	9.30E+08	7.17	1.21E+08	15.86
Feed Item 4	5.87E+08	4.53	8.43E+07	11.05
Feed Eff 1	4.65E+04	0.000	8.51E+05	0.11
Feed Eff 2	8.05E+05	0.006	6.10E+07	7.99
Feed Eff 3	1.48E+06	0.011	9.68E+07	12.69
Feed Eff 4	1.56E+06	0.012	8.87E+07	11.63
Wash 1	< 1.66E+06	< 0.013	8.26E+07	10.83
Wash 2	< 1.10E+06	< 0.008	3.62E+07	4.74
Wash 3	< 1.88E+06	< 0.014	7.70E+06	1.01
Wash 4	< 1.53E+06	< 0.012	2.65E+06	0.35
Wash 5	< 7.90E+05	< 0.006	1.07E+06	0.14
Wash 6	< 1.12E+06	< 0.009	6.89E+05	0.09
Wash 7	2.94E+06	0.023	4.99E+05	0.07
Wash 8	4.90E+06	0.038	3.65E+05	0.05
Heads 0.3	1.64E+07	0.126	2.68E+06	0.35
Heads 0.4	1.94E+07	0.150	2.37E+06	0.31
Heads 0.5	1.65E+07	0.127	2.16E+06	0.28
Heads 0.6	2.74E+07	0.211	3.28E+06	0.43
Heads 0.7	4.96E+08	3.82	5.71E+06	0.75
Heads 0.8	6.42E+09	49.5	1.19E+07	1.56
Heads	< 5.91E+07	< 0.456	2.60E+06	0.34
Product	5.81E+09	44.9	5.50E+06	0.72
Hearts 60	1.22E+09	9.41	< 2.27E+05	< 0.03
Hearts 55	5.50E+08	4.24	< 1.82E+05	< 0.02
Hearts 50	3.04E+08	2.34	1.45E+05	0.02
Hearts 45	1.32E+08	1.02	5.70E+04	0.01
Hearts 40	7.00E+07	0.540	4.54E+04	0.01
Hearts 35	3.75E+07	0.289	2.96E+04	0.00
Tails 1	1.49E+08	1.15	4.85E+04	0.01
Tails 2	7.51E+06	0.058	1.21E+04	0.00

Table A-2. Additional Anion Exchange Operating Data

Feed Bottle	Volume (mL)	Pu Height in Column (cm)	Effluent Dose Rate (mrem/h)
Feed Items 1-3	2250	13	3
Feed Item 4.1	2000	18	65
Feed Item 4.2	2000	24	105
Feed Item 4.3	2000	29	120
Feed Item 4.4	2000	33	135
Feed Item 4.5	2000	38	135
Feed Item 4.6	2000	42	140
Feed Item 4.7	2000	46	130
Feed Item 4.8	900	46.5	90
Wash 1	1000	NM	110
Wash 2	2000	53	75
Wash 3	2000	55	16
Wash 4	2000	58	5.1
Wash 5	2000	NM	2.2
Wash 6	2000	59	1.8
Wash 7	2000	NM	1.5
Wash 8	2000	60	1.2
Heads	1000	NM	4.5
Product	1760	NM	48
Tails 1	1000	NM	4.8
Tails 2	1900	NM	2.5
NM = not measured			

Table A-3. Comparison of Primary Feed and Raffinate Contents by ICP-ES

Element	Feed Item 4 (Primary Feed) (mg/L)	Primary Feed Raffinate (mg/L)
Al	4320	4540
B	1110	1160
Ba	1.83	1.61
Be	1.93	2.12
Ca	44.7	43.2
Cd	< 1.21	< 0.121
Ce	< 7.91	1.64
Co	< 1.83	0.728
Cr	42.2	44.4
Cu	9.41	6.52
Fe	1210	1250
Gd	< 3.84	< 1.92
K	1810	1880
Mg	40.1	41.8
Mn	7.1	8.01
Mo	< 16.4	4.38
Na	14300	14900
Ni	95.4	98
Pb	< 17.6	6.89
S	< 300	< 30
Si	< 21.5	6.73
Sn	<14.7	5.89
Sr	<0.2	0.194
Ti	1.29	1.74
Zn	3.56	2.55
Zr	< 0.63	0.747

Table A-4. Comparison of Primary Feed and Raffinate Contents by ICP-MS

Mass Number	Feed Item 4 (Primary Feed) (mg/L)	Primary Feed Raffinate (mg/L)
59	0.774	0.76
71	43.9	43.0
88	0.209	0.15
89	0.622	0.59
90	0.661	0.46
91	0.163	0.10
92	0.955	0.77
94	0.654	0.52
95	0.752	0.69
96	0.780	0.74
97	0.445	0.45
98	1.08	1.05
100	0.478	0.44
106	< 0.200	< 0.02
107	< 0.050	0.01
108	< 0.050	< 0.015
110	< 0.050	< 0.010
112	0.085	0.08
114	0.105	0.06
116	0.880	0.90
117	0.429	0.47
118	1.45	1.46
119	1.03	0.53
120	10.9	1.85
121	0.103	0.12
122	0.357	0.40
123	< 0.100	< 0.045
124	0.564	0.50

Note: highlighted cells indicate values below the method detection limit

Table A-5. Comparison of Primary Feed and Raffinate Contents by ICP-MS

Mass Number	Feed Item 4 (Primary Feed) (mg/L)	Primary Feed Raffinate (mg/L)
59	0.774	0.76
71	43.9	43.0
88	0.209	0.15
89	0.622	0.59
90	0.661	0.46
91	0.163	0.10
92	0.955	0.77
94	0.654	0.52
95	0.752	0.69
96	0.780	0.74
97	0.445	0.45
98	1.08	1.05
100	0.478	0.44
106	< 0.200	< 0.02
107	< 0.050	0.01
108	< 0.050	< 0.015
110	< 0.050	< 0.010
112	0.085	0.08
114	0.105	0.06
116	0.880	0.90
117	0.429	0.47
118	1.45	1.46
119	1.03	0.53
120	10.9	1.85
121	0.103	0.12
122	0.357	0.40
123	< 0.100	< 0.045
124	0.564	0.50
135	0.099	0.11
137	0.227	0.18
138	1.253	1.19
140	5.83	1.53
142	0.777	0.19
144	0.08	< 0.01
146	0.05	< 0.01
155	< 0.050	0.02
156	0.099	0.05
157	< 0.050	0.02
158	< 0.050	0.04
160	< 0.050	0.03
166	< 0.050	0.04
167	< 0.050	0.03

Note: highlighted cells indicate values below the method detection limit

Table A-4. Comparison of Primary Feed and Raffinate Contents by ICP-MS (continued)

Mass Number	Feed Item 4 (Primary Feed) (mg/L)	Primary Feed Raffinate (mg/L)
168	< 0.050	0.03
170	< 0.050	0.03
176	< 0.050	< 0.01
177	< 0.050	< 0.01
178	< 0.050	0.01
179	< 0.050	< 0.01
180	< 0.050	0.02
181	0.162	0.14
182	0.851	0.85
183	0.434	0.47
184	1.05	1.00
186	0.922	0.94
206	0.861	0.99
207	0.809	0.83
208	2.05	1.94
234	0.166	0.16
235	6.04	5.61
236	1.22	0.95
237	0.621	0.06
238	1.68	0.59
239	4416	7.66
240	283	0.46
241	15.0	13.10

Note: highlighted cells indicate values below the method detection limit

Table A-6. Uncertainties in MS Moisture Contents

Batch ID	MS Moisture Content, wt %	95% Confidence Interval	
		Lower Bound	Upper Bound
Demo 1a	0.30	0.28	0.33
Demo 1b	0.32	0.30	0.35
Demo 1c* [†]	> 0.42	0.39	0.45
Demo 1d*, Argon, Room Temp. for 1 h	0.26	0.25	0.28
Demo 1e*, Argon, ~50 °C for 1 h	0.37	0.34	0.39
Demo 1f*, Argon, ~93 °C for 1 h	0.44	0.41	0.48

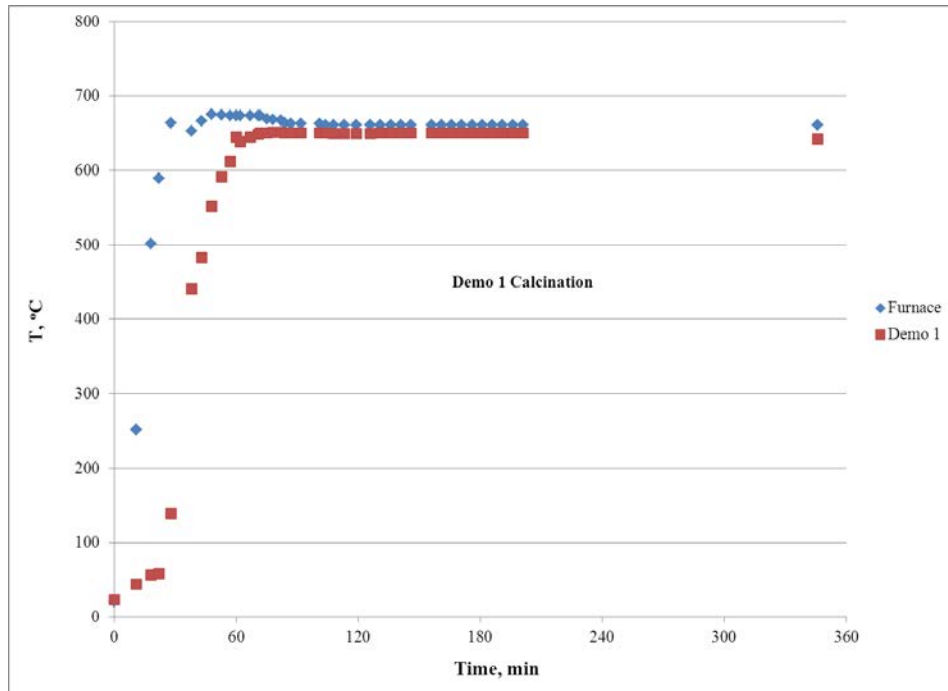


Figure A-1. Temperature Profiles for Demo 1 Calcination

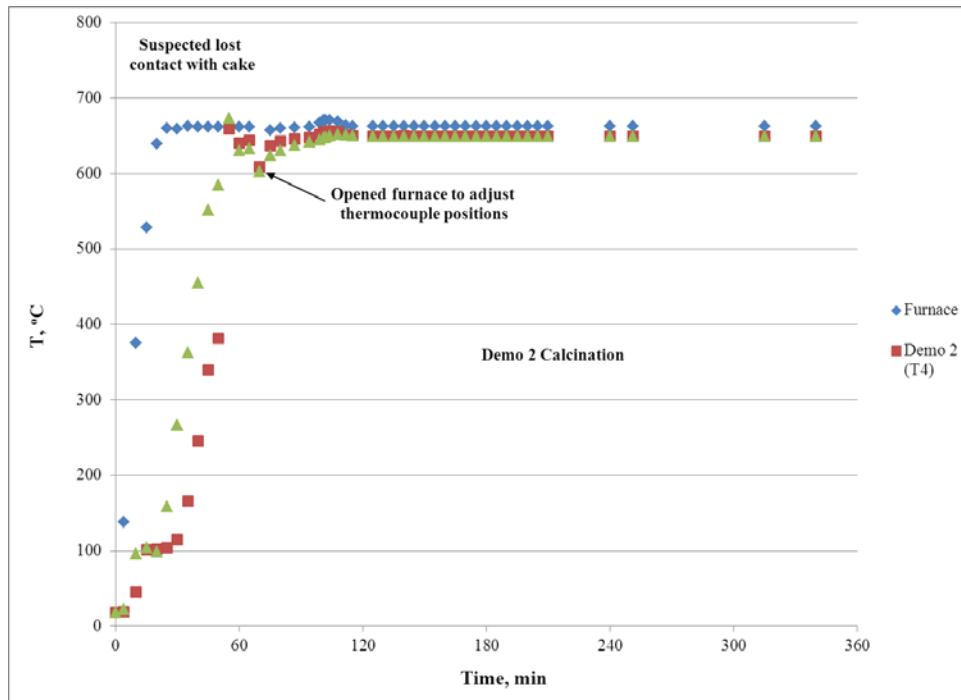


Figure A-2. Temperature Profiles for Demo 2 Calcination

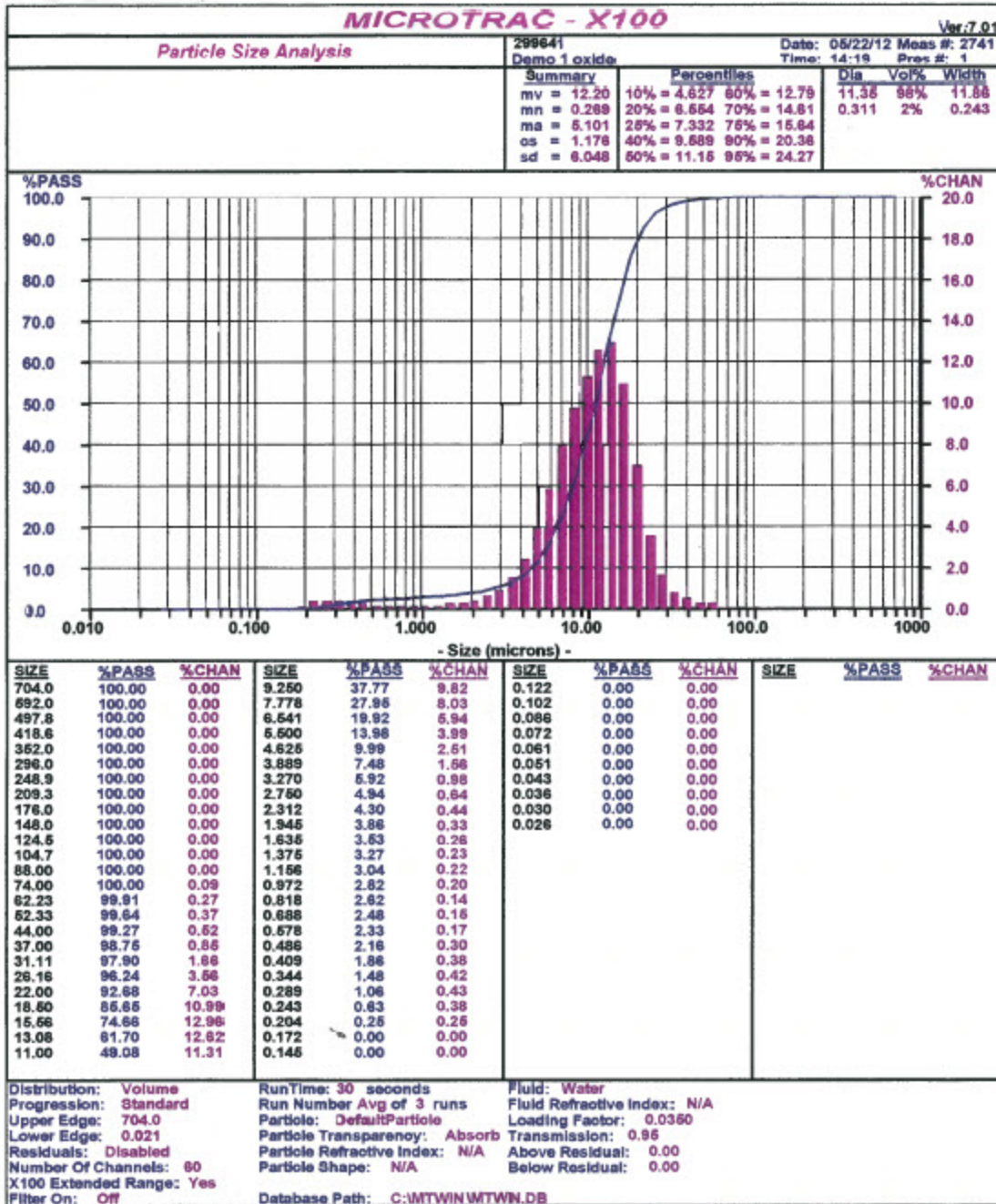


Figure A-3. Particle Size Analysis for Demo 1 PuO₂

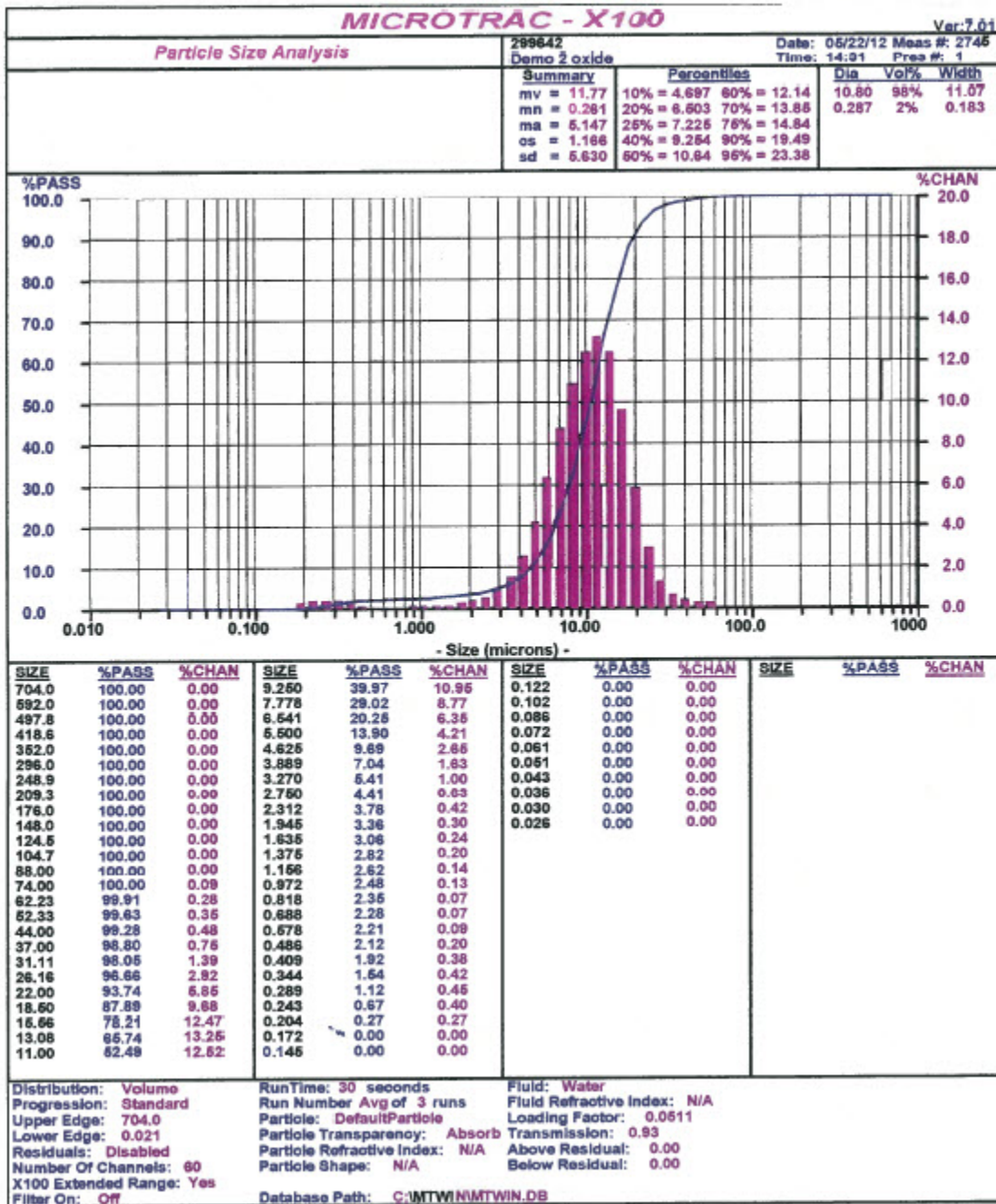


Figure A-4. Particle Size Analysis for Demo 2 PuO₂

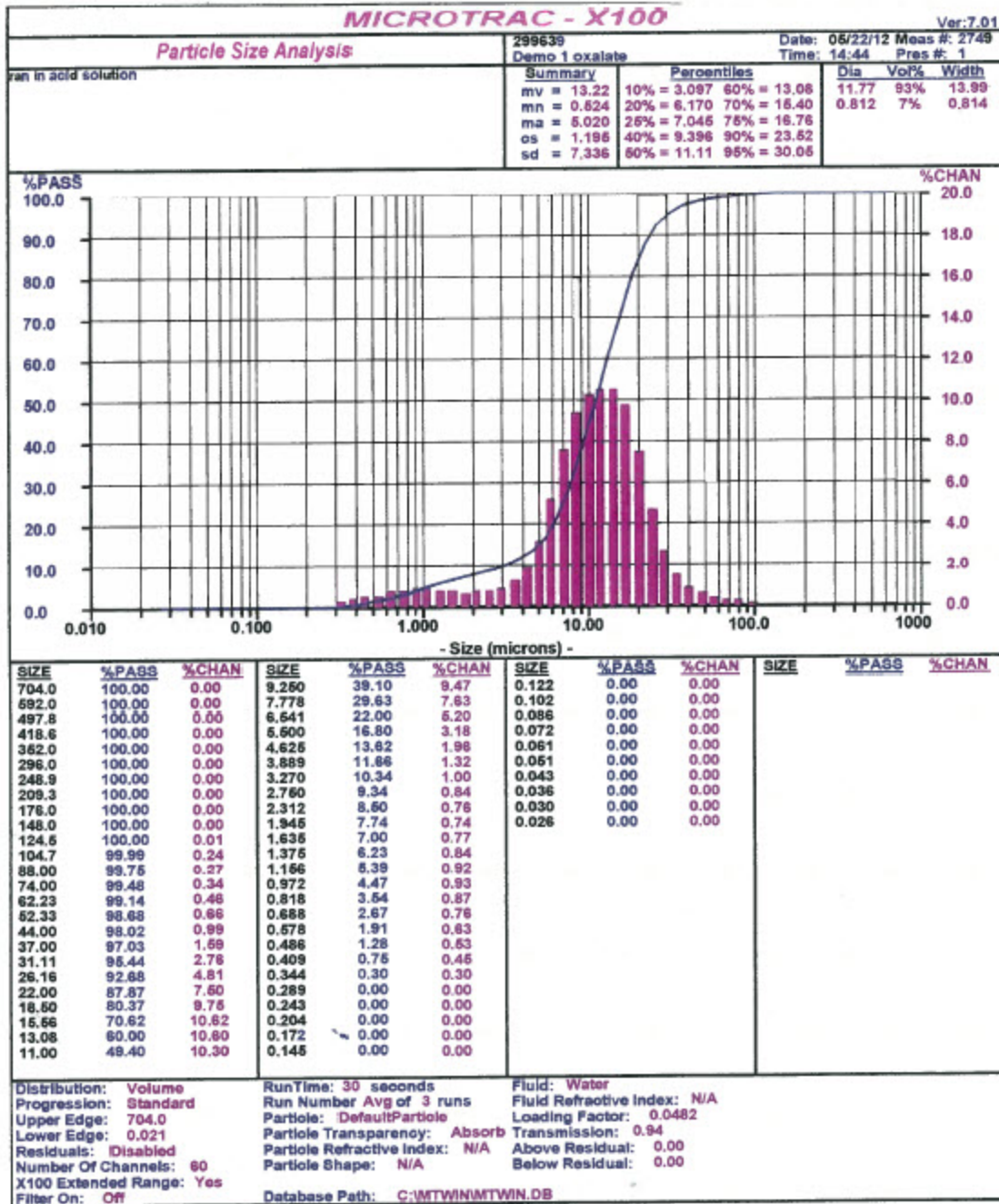


Figure A-5. Particle Size Analysis for Demo 1 Pu Oxalate

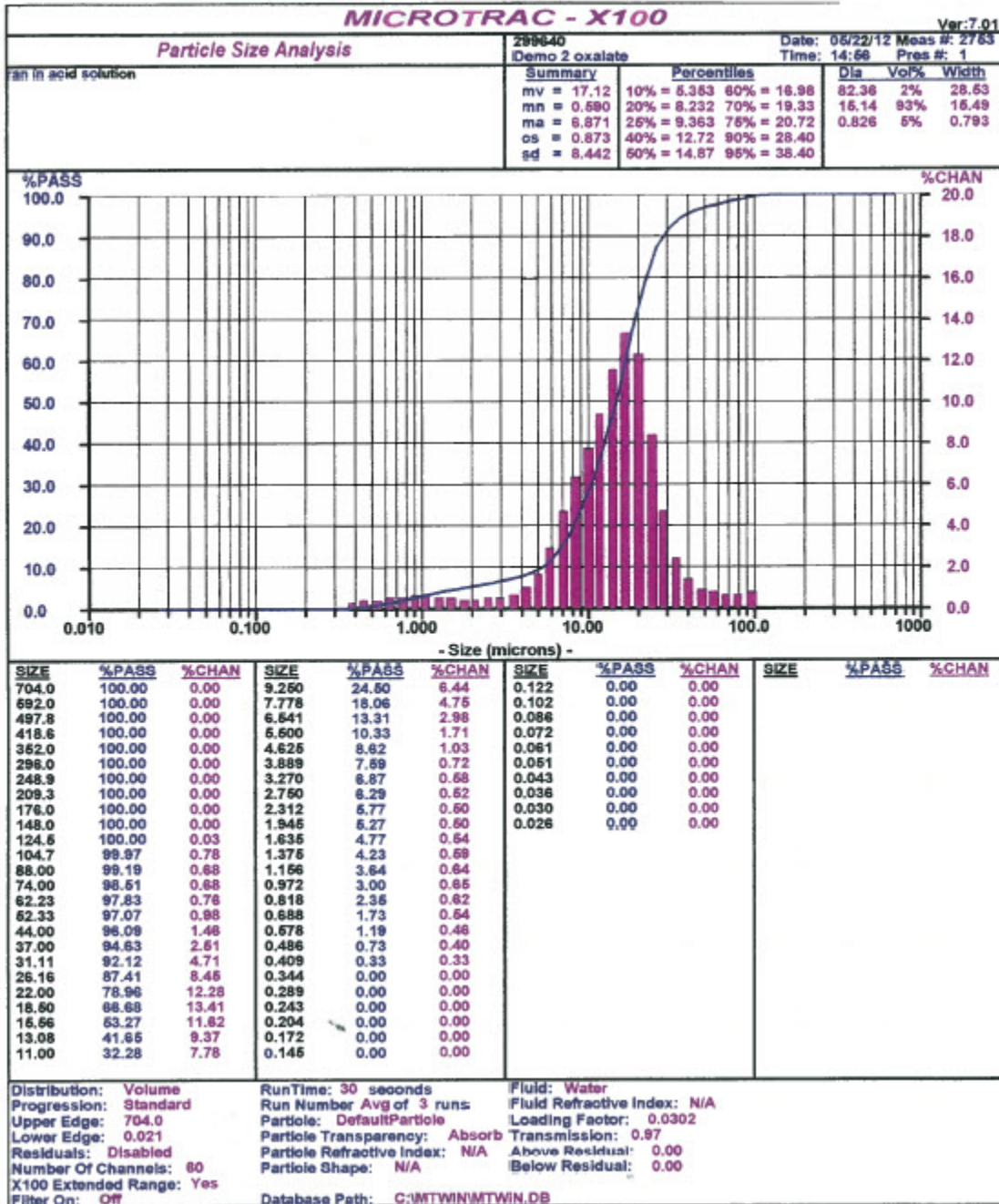


Figure A-6. Particle Size Analysis for Demo 2 Pu Oxalate

Table A-7. Analyses of Reagents by ICP-ES and Total Acid

Element	7 M Nitric Acid (mg/L)	0.9 M Oxalic Acid (mg/L)
Ag	< 0.106	< 0.106
Al	< 0.546	< 0.546
B	< 0.343	< 0.343
Ba	< 0.028	< 0.028
Ca	< 0.315	< 0.315
Cd	< 0.054	< 0.054
Ce	< 0.585	< 0.585
Co	< 0.129	< 0.129
Cr	< 0.067	< 0.067
Cu	< 0.124	< 0.098
Fe	< 0.114	0.0846
K	< 2.43	< 2.43
La	< 0.135	< 0.135
Li	< 0.057	< 0.057
Mg	< 0.254	< 0.254
Mn	< 0.019	< 0.019
Mo	< 0.162	< 0.162
Na	< 0.56	< 0.56
Nb	< 0.119	< 0.119
Nd	< 0.61	< 0.61
Ni	< 0.043	< 0.043
P	< 0.183	< 0.183
Pb	< 0.23	< 0.23
Re	< 4.06	< 0.811
S	< 0.735	< 0.735
Si	< 0.206	< 0.206
Sn	< 0.236	< 0.236
Sr	< 0.008	< 0.008
Ti	< 0.048	< 0.048
V	< 0.043	< 0.043
Zn	< 0.083	< 0.083
Zr	< 0.043	< 0.043
Total Acid, M	7.04	NM

Note: highlighted cells indicate values above the method detection limit.
NM = Not Measured

Table A-8. Analyses of Reagents by ICP-MS

Mass Number	7 M Nitric Acid (µg/L)	0.9 M Oxalic Acid (mg/L)
51	< 5.00E-01	< 1.50E+00
59	< 3.50E-01	< 2.00E-01
69	< 1.00E-01	< 1.50E-01
71	< 1.50E-01	< 1.00E-01
82	< 8.55E+00	< 1.86E+01
84	< 1.60E+00	< 3.95E+00
85	< 5.50E-01	< 1.00E-01
86	< 4.00E-01	< 4.00E-01
87	< 1.00E-01	< 3.00E-01
88	< 2.00E-01	< 1.00E-01
89	< 1.50E-01	< 1.00E-01
90	< 2.50E-01	< 1.00E-01
91	< 1.00E-01	< 2.00E-01
92	< 1.00E-01	< 4.00E-01
93	< 1.00E-01	7.45E-01
94	< 6.00E-01	< 2.00E-01
95	< 3.00E-01	< 3.00E-01
96	< 4.50E-01	< 3.00E-01
97	< 4.50E-01	< 2.00E-01
98	< 1.50E-01	< 4.00E-01
99	< 1.50E-01	< 1.50E-01
100	< 1.50E-01	< 2.00E-01
101	< 1.00E-01	< 1.50E-01
102	< 2.00E-01	< 2.50E-01
103	< 1.00E-01	< 2.00E-01
104	< 1.00E-01	< 1.00E-01
105	< 1.00E-01	< 1.50E-01
106	< 1.00E-01	< 1.00E-01
107	< 1.50E-01	< 1.50E-01
108	< 1.50E-01	< 1.50E-01
109	< 1.00E-01	< 2.00E-01
110	< 1.00E-01	< 2.50E-01
111	< 2.50E-01	< 1.00E-01
112	< 2.00E-01	< 1.50E-01
113	< 2.65E+00	< 2.60E+00
114	< 2.50E-01	< 1.00E-01
116	1.67E-01	< 1.00E-01
117	1.05E-01	< 1.00E-01
118	2.55E-01	< 1.00E-01
119	< 1.50E-01	< 2.00E-01
120	3.09E-01	< 2.00E-01
121	< 2.50E-01	< 1.00E-01
122	< 2.50E-01	< 1.00E-01
123	< 1.50E-01	< 1.00E-01

Table A-7. Analyses of Reagents by ICP-MS (continued)

Mass Number	7 M Nitric Acid (µg/L)	0.9 M Oxalic Acid (mg/L)
124	< 2.50E-01	< 2.50E-01
125	< 5.50E-01	< 1.50E-01
126	< 5.50E-01	< 5.00E-01
128	< 7.00E-01	< 1.50E+00
130	< 2.90E+00	< 6.50E-01
133	< 5.00E-01	< 2.50E-01
134	< 2.00E-01	< 3.40E+00
135	< 1.50E-01	< 1.00E-01
136	< 6.50E-01	< 1.05E+00
137	< 1.00E-01	< 1.00E-01
138	< 1.00E-01	< 1.00E-01
139	< 1.00E-01	< 1.00E-01
140	1.87E-01	1.20E+00
141	< 2.00E-01	< 1.00E-01
142	< 1.00E-01	< 2.00E-01
143	< 1.00E-01	< 1.00E-01
144	< 1.00E-01	< 1.00E-01
145	< 1.00E-01	< 1.00E-01
146	< 1.00E-01	< 1.00E-01
147	< 1.00E-01	< 1.00E-01
148	< 1.00E-01	< 1.00E-01
149	< 1.00E-01	< 1.00E-01
150	< 1.50E-01	< 1.00E-01
151	< 1.00E-01	< 1.00E-01
152	< 1.00E-01	< 1.00E-01
153	< 1.00E-01	< 1.00E-01
154	< 1.00E-01	< 1.00E-01
155	< 1.50E-01	< 1.00E-01
156	< 1.00E-01	< 1.00E-01
157	< 1.00E-01	< 1.00E-01
158	< 1.00E-01	< 1.00E-01
159	< 2.00E-01	< 1.00E-01
160	< 1.00E-01	< 1.00E-01
161	< 1.00E-01	< 1.00E-01
162	< 1.00E-01	< 2.00E-01
163	< 1.00E-01	< 1.00E-01
164	< 1.00E-01	< 1.50E-01
165	< 1.00E-01	< 1.00E-01
166	< 1.00E-01	< 1.00E-01

Table A-7. Analyses of Reagents by ICP-MS (continued)

Mass Number	7 M Nitric Acid (µg/L)	0.9 M Oxalic Acid (mg/L)
167	< 1.00E-01	< 1.00E-01
168	< 1.00E-01	< 1.00E-01
169	< 1.00E-01	< 1.00E-01
170	< 1.00E-01	< 1.00E-01
171	< 1.00E-01	< 1.00E-01
172	< 1.00E-01	< 1.00E-01
173	< 1.00E-01	< 1.00E-01
174	< 1.00E-01	< 1.00E-01
175	< 1.00E-01	< 1.00E-01
176	< 1.00E-01	< 1.00E-01
177	< 1.00E-01	< 1.00E-01
178	< 1.00E-01	< 1.00E-01
179	< 1.00E-01	< 1.00E-01
180	< 1.00E-01	< 1.50E-01
181	< 1.00E-01	2.10E+00
182	< 1.00E-01	< 1.00E-01
183	< 1.00E-01	< 1.00E-01
184	< 1.00E-01	< 1.00E-01
185	< 1.00E-01	< 1.00E-01
186	< 1.00E-01	< 1.00E-01
187	< 1.00E-01	< 1.00E-01
191	1.72E-01	< 3.00E-01
193	1.90E-01	< 3.00E-01
194	< 3.00E-01	< 1.50E-01
195	< 1.50E-01	< 2.50E-01
196	< 1.50E-01	< 1.00E-01
197	< 6.00E-01	< 7.00E-01
198	< 1.00E-01	< 1.00E-01
203	< 2.00E-01	< 1.00E-01
204	< 1.00E-01	< 1.00E-01
205	< 5.00E-01	< 1.00E-01
206	1.97E-01	< 1.50E-01
207	1.81E-01	< 1.50E-01
208	4.09E-01	< 2.00E-01
232	< 1.50E-01	< 1.00E-01
235	< 2.00E-01	< 1.00E-01
238	4.71E+00	< 2.00E-01

Distribution:

S. D. Fink, 773-A
K. M. Fox, 999-W
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
E. A. Kyser, 773-A
T. S. Rudisill, 773-A
R. A. Pierce, 773-A
J. H. Scogin, 773-A
M. C. Thompson, 773-A
W. D. King, 773-42A
C. A. Nash, 773-42A
M. L. Crowder, 773-A
K. M. L. Taylor-Pashow, 773-A
S. L. Garrison, 704-2H

Records Administration (EDWS)

C. Wilson, 773-A

W. E. Harris, 704-2H
J. B. Schaade, 704-2H
G. J. Zachman, 225-7H
P. B. Andrews, 704-2H
S. J. Howell, 221-H
W. G. Dyer, 704-2H
M. J. Swain, 703-H
M. J. Lewczyk, 221-H
J. L. O'Conner, 704-2H
S. L. Hudlow, 221-H
W. H. Clifton, 704-2H
K. P. Burrows, 704-2H
K. J. Gallahue, 221-H
J. E. Therrell, 704-2H
J. W. Christopher, 704-2H
J. E. Elkourie, 704-2H
R. H. Smith, 704-2H
R. R. Livingston, 730-2B
D. Stimac, 730-2B
J. W. McClard, 705-K
S. A. Thomas, 703-46A