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## **Dissolution of 3013-DE Sample 10-16**

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## EXECUTIVE SUMMARY

The HB-Line Facility has a long-term mission to dissolve and disposition legacy fissile materials. HB-Line dissolves plutonium dioxide ( $\text{PuO}_2$ ) from K-Area parting support of the 3013 Destructive Examination (DE) program.<sup>a</sup> The  $\text{PuO}_2$ -bearing solids originate from a variety of unit operations and processing facilities, but all of the material is assumed to be high-fired (i.e., calcined in air for a minimum of two hours at  $\geq 750^\circ\text{C}$ ).

The Savannah River National Laboratory (SRNL) conducted dissolution flowsheet studies on 3013 DE Sample 10-16 (can R610826), which contains weapons-grade plutonium (Pu) as the fissile material. The dissolution flowsheet study was performed for 4 hours at  $108^\circ\text{C}$  on unwashed material using 12 M nitric acid ( $\text{HNO}_3$ ) containing 0.20 M potassium fluoride (KF). After 4 hours at  $108^\circ\text{C}$ , the  $^{239}\text{Pu}$  Equivalent concentration was 32.5 g/L (gamma, 5.0% uncertainty). The insoluble residue comprised 9.88 wt % of the initial bulk weight, and contained 5.31 – 5.95 wt % of the initial Pu. The residue contained Pu in the highest concentration, followed by tungsten (W).

Analyses detected 2,770 mg/L chloride ( $\text{Cl}^-$ ) in the final dissolver solution (3.28 wt %), which is significantly lower than the amount of  $\text{Cl}^-$  detected by prompt gamma (9.86 wt %) and the 3013 DE Surveillance program (14.7 wt %). A low bias in chloride measurement is anticipated due to volatilization during the experiment. Gas generation studies found approximately 60 mL of gas per gram of sample produced during the first 30 minutes of dissolution. Little to no gas was produced after the first 30 minutes. Hydrogen gas ( $\text{H}_2$ ) was not detected in the sample. Based on detection limits and accounting for dilution, the generated gas contained  $< 0.12$  vol %  $\text{H}_2$ , which is well below the 4.0 vol % flammability limit for  $\text{H}_2$  in air.

Filtration of the dissolver solution occurred readily. When aluminum nitrate nonahydrate (ANN) was added to the filtered dissolver solution at a 3:1 Al:F molar ratio, and stored at room temperature for 24 hours, the solution filtered approximately 6 times slower than when filtered 30 minutes after ANN addition, requiring 6 minutes to complete compared to 55 seconds for the first filtration. It is likely that the ambient-temperature solubility for ANN was exceeded.

A 4-hour dissolution time at a temperature of  $108^\circ\text{C}$  in 12 M  $\text{HNO}_3$ /0.2 M KF is recommended for dissolution of this material.

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<sup>a</sup> Recently, DOE issued guidance suspending the dissolution program. This flowsheet, in progress at the time of that decision, is being documented for later use.

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## **LIST OF ABBREVIATIONS**

ANN	aluminum nitrate nonahydrate
DE	destructive examination
GC	gas chromatography
IC	ion chromatography
ICP-ES	inductively coupled plasma – emission spectroscopy
ICP-MS	inductively coupled plasma – mass spectroscopy
MC&A	material control and accountability
rpm	revolutions per minute
SRNL	Savannah River National Laboratory
TGA-MS	thermogravimetric analysis – mass spectroscopy
XRD	X-ray diffraction

## 1.0 Introduction

### 1.1 HB-Line Flowsheet

The HB-Line Facility has a long-term mission to dissolve fissile materials and disposition them. HB-Line dissolves PuO<sub>2</sub> coming from K-Area in support of the 3013 DE program. (DOE recently suspended such processing in HB-Line; SRNL is documenting this study in progress at the time of that program decision.) The PuO<sub>2</sub> is from various unit operations and processing facilities throughout the DOE complex, but all of the material has been calcined for a minimum of two hours at  $\geq 750$  °C, in accordance with the requirements of the Department of Energy standard for the packaging and long-term storage of plutonium materials (DOE-STD-3013).<sup>[1]</sup>

To support the dissolution of these materials in HB-Line, SRNL conducted testing to validate an existing dissolution flowsheet. The original objective of flowsheet testing was to dissolve 3013 DE materials to ~70 g/L Pu with less than 5% of the Pu remaining in the solid residue.<sup>[2]</sup> As a result, the recommended flowsheet included the use of 12 M nitric acid (HNO<sub>3</sub>) and 0.2 M potassium fluoride (KF) at 112-114 °C for 12 hours. The flowsheet requirements were modified to 12 M HNO<sub>3</sub> and 0.2 M KF for 12 hours at 108 °C to produce a final concentration containing ~47 g/L of dissolved fissile material.<sup>[3]</sup> The current objective is to produce a product with a Pu concentration of 30-35 g/L while minimizing the corrosion impact to the dissolver and associated equipment.<sup>[4]</sup> To meet this objective, the dissolution protocol was further modified to dissolve in 12 M HNO<sub>3</sub> containing 0.20 M KF at 108 °C for 4 hours.

The primary objectives of the present study are to test the flowsheet for dissolution efficacy, identify and characterize gases generated during the dissolution process, and to characterize the behavior of the dissolver solution after the addition of ANN (results of an earlier investigation indicate the potential for precipitation subsequent to ANN addition).<sup>[5]</sup>

### 1.2 Background Sample Information

Dissolution flowsheet studies were performed on Sample 10-16, Vial B366 (Source Item R610826). Prompt gamma analyses of the material measured in K-Area are listed in Table 1-1; prompt gamma count times are typically 60 minutes.

**Table 1-1. Prompt Gamma Data for Parent 3013 Cans for Sample 10-16.**

Al (wt %)	ND	Mg (wt %)	1.71
Be (wt %)	0.054	Na (wt %)	2.97
Cl (wt %)	9.86	K (wt %)	4.22
F (wt %)	0.333		
ND = not detected			

Prior analysis of the samples for the DE surveillance program yielded the results in Table 1-2.



**Table 1-2. Sample 10-16 Characterization Data from 3013 DE Surveillance Program.**

Major Compound(s) XRD <sup>[6]</sup>	PuO <sub>2</sub>		
Minor Compound(s) XRD <sup>[6]</sup>	NiO, NaCl, KCl		
ICPES Data: <sup>[7]</sup>			
Ag (μg/g)	< 119	Mg (μg/g)	12,800
Al (μg/g)	364	Mn (μg/g)	192
Ba (μg/g)	< 94.8	Mo (μg/g)	< 201
Be (μg/g)	1305	Na (μg/g)	42,400
Ca (μg/g)	5,865	Ni (μg/g)	8,960
Cd (μg/g)	< 124	Pb (μg/g)	< 467
Cr (μg/g)	870	Sn (μg/g)	< 551
Cu (μg/g)	< 792	Ti (μg/g)	137
Fe (μg/g)	3,685	U (μg/g)	< 9,710
K (μg/g)	65,250	Zn (μg/g)	381
La (μg/g)	< 103	Zr (μg/g)	< 142
IC Data: <sup>[8]</sup>			
F <sup>-</sup> (μg/g)	< 301	PO <sub>4</sub> <sup>3-</sup> (μg/g)	< 150
Cl <sup>-</sup> (μg/g)	146,500	SO <sub>4</sub> <sup>2-</sup> (μg/g)	1,145
NO <sub>3</sub> <sup>-</sup> (μg/g)	80		

## 2.0 Experimental Procedure

### 2.1 Test Methods

A single dissolution test was performed. The sample was not washed (to remove Cl<sup>-</sup>) prior to testing. The dissolution test used 12 M HNO<sub>3</sub> and 0.2 M KF at 108 °C for 4 hours. A list of the process conditions is contained in Table 2-1.

**Table 2-1. Dissolution Test Parameters.**

DE Sample	HNO <sub>3</sub> (M)	KF (M)	Liquid Vol. (mL)	Sample wt (g)	Fissile (g)*	Vial #
10-16	12	0.2	100	7.590	4.00	B-366
* Based on material control and accountability (MC&A) data.						

The dissolution was performed using a borosilicate flask fitted with a reflux condenser to minimize evaporative losses. The total volume of the flask and the condenser is 180 mL. Operationally, the dissolution test was performed as follows. The amount of bulk sample specified in Table 2-1 was added to the empty test vessel. The dissolver solution was added on top of the solids along with a stir bar. The dissolver head space was purged with argon (Ar) by connecting the vessel to the Ar supply plumbed into the glovebox. After purging, the Ar gas service was disconnected and an empty 1-L gas collection bag was connected to the apparatus. The dissolver was then sealed to isolate it from the glovebox atmosphere.

The hot plate was turned on and set to control the vessel liquid temperature at 108 °C. The stirrer was turned on at 250 rpm (revolutions per minute). The temperature of the system reached 108 °C within 15 minutes. Thirty minutes after reaching temperature the first gas collection bag was removed and an empty gas collection bag was attached to the system. The volume of gas collected was measured by water displacement, and a sample of the gas was collected for gas

chromatography (GC) analysis. To obtain a sample of gas for GC, the gas collection bag was connected to a 25-mL gas sample bulb that had previously been purged with Ar and evacuated. The gas bag was then opened to the sample bulb and the sample was drawn into the gas sample bulb. After the first 30 minutes no additional gas generation was observed. The second gas collection bag was left on for the remainder of the dissolution to maintain a closed system, although no additional gas was being produced.

After 1 hour at 108 °C, the first liquid sample was removed. Five minutes prior to each sampling event (at 1, 2, 3, and 4 hours) the stirring was stopped to allow any solids to settle. Aliquots (0.5 mL) were then removed and diluted with an additional 0.5 mL of 12 M HNO<sub>3</sub>/0.2 M KF solution. Stirring was resumed immediately after sampling.

After 4 hours at 108 °C, the heating and stirring were stopped and the solution was allowed to cool. After cooling to approximately 50 °C, the 4-hour samples were removed, and the solution was then filtered through a 5-micron filter paper; 92 mL of filtrate was collected. The solids on the filter were dried in air for 5 days and weighed.

The filtrate (92 mL) was combined with 26 mL of 2.1 M ANN. Thirty minutes after the addition of ANN to the dissolver solution, the solution was filtered through a 5-micron filter paper. Filtration was rapid, completing in less than one minute. Twenty-four hours after the addition of ANN to the dissolver solution, the solution was filtered again through a 5-micron filter paper. The solution filtered about 6 times slower than when filtered 30 minutes after ANN addition, requiring 6 minutes to complete.

The filter paper containing the residue from the first filtration (before ANN addition) was placed in a zirconium (Zr) metal crucible. The crucible was then heated at 600 °C in a muffle furnace for 15 minutes to combust the filter paper. After cooling the crucible was reweighed to determine the mass of the residue (0.4489 g). Then, 3.7326 g of sodium peroxide (Na<sub>2</sub>O<sub>2</sub>) was added to the crucible. The crucible and contents were heated to 700 °C in a muffle furnace and held at temperature for 57 minutes. After the crucible cooled, aliquots (~15 mL) of 4 M HNO<sub>3</sub> were added to the crucible to dissolve the residue. After each addition of 4 M HNO<sub>3</sub> the contents of the crucible were decanted and filtered through a 5-micron filter paper. After all the residue had been dissolved and filtered, the solution volume was measured and samples were removed for gamma scan, ICP-MS, and ICP-ES analyses. The final volume of recovered solution was 43 mL. After drying in air for 4 days a small amount (0.2085 g) of light colored solid was observed on the filter paper. The solid was not analyzed.

## 2.2 Analytical Methods

Table 2-2 is a tabulation of the samples collected during the experiment and submitted for analysis.

**Table 2-2. Dissolution Test Sample Analyses.**

Total Time at 108 °C	Sample Analyses
30 min	<i>Gas:</i> generation volume; GC
1 h	<i>Liquid:</i> ICP-MS, gamma spectroscopy
2 h	<i>Liquid:</i> ICP-MS, gamma spectroscopy
3 h	<i>Liquid:</i> ICP-MS, gamma spectroscopy
4 h	<i>Liquid:</i> ICP-MS, gamma spectroscopy, ICP-ES, IC anions, total acid, free acid
Residue Fusion	<i>Liquid:</i> ICP-MS, gamma spectroscopy, ICP-ES
GC = gas chromatography ICP-MS = inductively coupled plasma – mass spectroscopy ICP-ES = inductively coupled plasma – emission spectroscopy IC = anion concentrations using ion chromatography All samples for ICP-MS and gamma spectroscopy (except residue fusion samples) were diluted by a factor of 2 prior to analysis.	

### 3.0 Results and Discussion

#### 3.1 Results

##### 3.1.1 Dissolver Solution Data

The data for samples collected at 1, 2, 3, and 4 hours for analyses by ICP-MS and gamma spectroscopy are provided in Appendix A along with notations regarding measurement uncertainty. The actinide concentration results are shown in Table 3-1, ICP-ES results are shown in Table 3-2, and other liquid sample results are shown in Table 3-3.

**Table 3-1. Pu, <sup>235</sup>U, and <sup>241</sup>Am Data for Sample 10-16.**

Analysis	1 h (g/L)	2 h (g/L)	3 h (g/L)	4 h*(g/L)
<sup>239</sup> Pu (gamma)	24.5	24.1	23.8	30.6
<sup>239</sup> Pu (ICPMS)	26.2	26.2	26.6	31.8
<sup>239</sup> Pu+ <sup>240</sup> Pu (gamma) <sup>#</sup>	26.0	25.6	25.3	32.5
<sup>239</sup> Pu+ <sup>240</sup> Pu (ICPMS)	27.7	27.8	28.3	33.7
<sup>235</sup> U (ICPMS)	0.061	0.077	0.072	0.071
<sup>241</sup> Am (gamma)	0.066	0.067	0.067	0.086
Eq. <sup>239</sup> Pu (ICPMS) <sup>†</sup>	27.8	27.9	28.3	33.7
* Final solution volume = 92 mL <sup>#</sup> Calculated using gamma <sup>239</sup> Pu results, with ICPMS determined isotopic ratio. <sup>†</sup> Eq <sup>239</sup> Pu = Total Pu + 0.65 x <sup>235</sup> U ICPMS uncertainty = ± 20% Gamma uncertainty = ± 5.0%				

**Table 3-2. ICP-ES Dissolution Data for Sample 10-16.**

Analyte LIMS #	Post-Dissolution (4 h) 300282331	Calculated Based on Table 1-2*	Na <sub>2</sub> O <sub>2</sub> Fusion 300282711
Ag (mg/L)	< 1.07	< 9.03	< 1.07
Al (mg/L)	155	27.6	139
Ba (mg/L)	4.98	< 7.20	8.95
Be (mg/L)	118	99.1	5.64
Ca (mg/L)	400	445	104
Cd (mg/L)	4.37	< 9.37	< 0.64
Cr (mg/L)	66	66	338
Cu (mg/L)	144	< 60.1	9.08
Fe (mg/L)	298	280	136
K (mg/L)	13100 <sup>^</sup>	12800 <sup>^</sup>	139
La (mg/L)	< 0.32	< 7.78	< 0.5
Mg (mg/L)	1110	972	221
Mn (mg/L)	20.2	14.6	2.57
Mo (mg/L)	< 2.14	< 15.2	8.54
Na (mg/L)	3180	3220	43600 <sup>†</sup>
Ni (mg/L)	844	680	316
Pb (mg/L)	< 20.4	< 35.5	< 3.66
Sn (mg/L)	22.6	< 41.8	13.5
Th (mg/L)	436	NM	< 11.8
Ti (mg/L)	6.56	10.4	9.77
U (mg/L)	458	< 737	< 27.6
Zn (mg/L)	38.7	28.9	4.63
Zr (mg/L)	< 0.235	< 10.8	2930 <sup>‡</sup>
ICP-ES uncertainty = ±10% *Assuming 100% dissolution. <sup>^</sup> Including K from starting solution (0.2 M KF) <sup>†</sup> Batch chemical used for fusion. <sup>‡</sup> Zr crucible used for fusion and dissolution.			

**Table 3-3. Other Data for Sample 10-16 (Post Dissolution).**

Analyte	LIMS #	Method	4 hour Measured (% unc.)
Cl <sup>-</sup> (µg/mL)	300282332	IC	2770 (10)
F <sup>-</sup> (µg/mL)	300282332	IC	3690 (10)
SO <sub>4</sub> <sup>2-</sup> (µg/mL)	300282332	IC	287 (10)
NO <sub>3</sub> <sup>-</sup> (µg/mL)	300282332	IC	730000 (10)
Free H <sup>+</sup> (M)	300282333	Free Acid	10.645 (10)
Total H <sup>+</sup> (M)	300282333	Total Acid	11.6 (10)

### 3.1.2 Dissolver Off-Gas Data

Table 3-4 contains the gas generation data. A significant amount of gas was generated during the first 30 minutes at 108 °C. The gas was brownish which implies the presence of nitrogen dioxide (NO<sub>2</sub>). Analysis of the gas sample indicated air had leaked into the dissolver head space or sample bulb after the argon purge. After the first 30 minutes, no noticeable gas was produced.

**Table 3-4. Gas Generation Data for 10-16 Dissolution.**

Time at 108 °C (min)	Volume (mL)	H <sub>2</sub> vol % (% Unc.)	N <sub>2</sub> vol % (% Unc.)	O <sub>2</sub> vol % (% Unc.)
0-30	450	< 0.1	78 (10)	21 (10)

### 3.1.3 Residual Solids

After the initial 4-hour dissolution for Sample 10-16, there was 0.750 g (9.88 wt %) of residue remaining. A portion of the residue (0.4489 g) was fused with Na<sub>2</sub>O<sub>2</sub> and dissolved in 4 M HNO<sub>3</sub>. The resulting solution (43 mL) was analyzed using gamma spectroscopy, ICP-MS, and ICP-ES. Based on the gamma results, the dissolved Na<sub>2</sub>O<sub>2</sub> fusion product contained 2.41 g/L total Pu. The ICP-MS results indicated a total Pu concentration of 2.82 g/L. From these results, it was determined that 0.17 g (gamma) – 0.20 g (ICP-MS) of Pu remained in the residue, and 3.09 g (gamma) – 3.21 g (ICP-MS) Pu dissolved into solution, meaning ~ 5.31% - 5.95% of the Pu remained in the residue after dissolution.

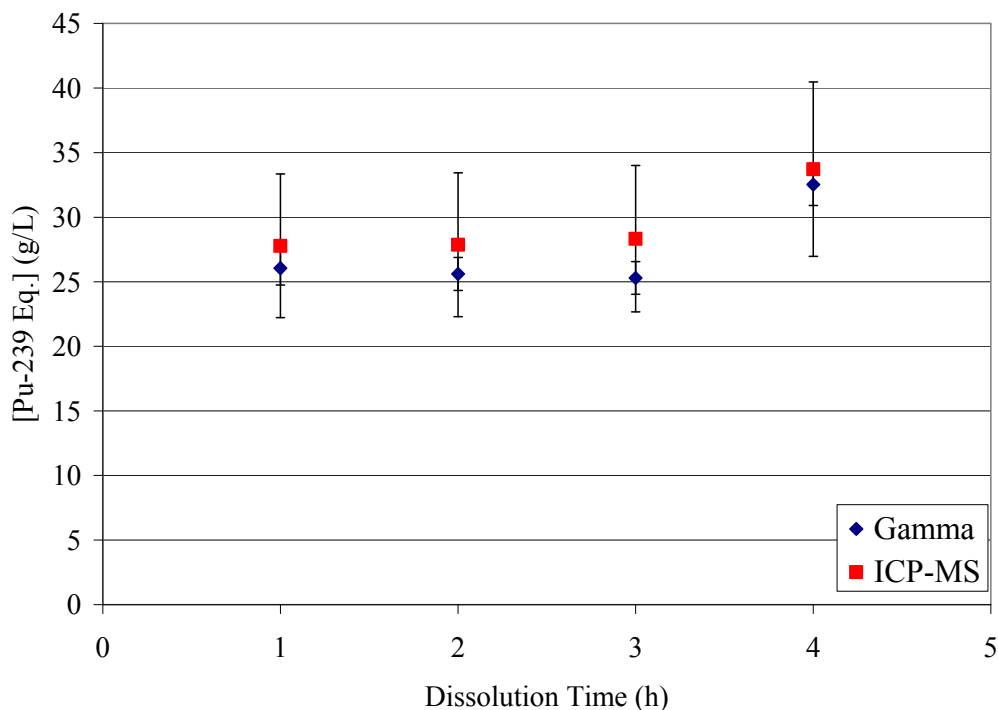
The ICP-MS and ICP-ES analyses of the residue also showed significant quantities tungsten (W, 763 mg/L); moderate quantities (221-348 mg/L) of chromium (Cr), magnesium (Mg), nickel (Ni), and tantalum (Ta); along with even lesser amounts (< 140 mg/L) of aluminum (Al), calcium (Ca), iron (Fe), potassium (K), and tin (Sn). Data for boron (B) and silicon (Si) are omitted as their presence can be attributed to the use of glass sample vials. Sodium (Na) and Zr are also omitted from Table 3-6 as their presence is due to the addition of Na<sub>2</sub>O<sub>2</sub> for the fusion and the use of a Zr crucible, respectively. Elements present at below 0.1 wt % were also omitted from Table 3-6 (see Table 3-6 for concentration data).

**Table 3-5. Concentration Data from Residue Dissolution using Na<sub>2</sub>O<sub>2</sub> Fusion.**

Analyte	Method	mg/L (% unc)	wt % (% unc)
<sup>239</sup> Pu	gamma	2260 (5)	21.7 (5)
<sup>239</sup> Pu	ICP-MS	2650 (20)	25.4 (20)
Al	ICP-ES	139 (10.1)	1.33 (10.1)
Ca	ICP-ES	104 (10)	1.00 (10)
Cr	ICP-ES	338 (10)	3.24 (10)
Fe	ICP-ES	136 (10)	1.30 (10)
K	ICP-ES	139 (10)	1.33 (10)
Mg	ICP-ES	221 (10)	2.12 (10)
Ni	ICP-ES	316 (10)	3.03 (10)
Sn	ICP-ES	13.5 (10.6)	0.13 (10.6)
Ta	ICP-MS	348 (20)	3.33 (20)
W	ICP-MS	763 (20)	7.31 (20)

## 3.2 Discussion

The Pu dissolution results for sample 10-16 (from Table 3-1) are graphed in Figure 1. The error bars show the analytical uncertainties of 20% and 5%, for ICP-MS and gamma spectroscopy, respectively. The flowsheet targeted a <sup>239</sup>Pu Eq. concentration of 40 g/L. Both the gamma and ICP-MS data indicate that the majority of the sample dissolved rapidly, reaching <sup>239</sup>Pu Eq. concentration of 26.1 g/L (gamma) – 27.8 g/L (ICP-MS) after 1 hour. There is little change in the Pu concentration through the next two sampling events; however, an increase in concentration is seen in the 4-hour sample. The <sup>239</sup>Pu Eq. concentration after 4 hours of dissolution was measured to be 32.5 g/L (gamma) – 33.7 g/L (ICP-MS). This data indicates that the full 4 hours of dissolution is necessary to achieve sufficient dissolution.



**Figure 1. Pu Dissolution Data for 10-16.**

The ICP-ES data for potassium ( $K^+$ ) in Sample 10-16 showed a concentration of 13.1 g/L, or 0.335 M. This value is about 102% of the calculated value combining the  $K^+$  in the dissolver solution (0.2 M, 7.82 g/L) and the amount of  $K^+$  measured in the sample from the 3013 DE Surveillance program (65.25 mg/g). The calculated concentration is 12.8 g/L.

Prompt gamma analysis of sample 10-16 revealed 9.86 wt %  $Cl^-$  and during the DE Surveillance program analyses, 146,500  $\mu\text{g/g}$   $Cl^-$  (14.65 wt %) were detected in this material. After 4 hours of dissolution the  $Cl^-$  concentration of the solution was 2,770  $\mu\text{g/mL}$ . This corresponds to 32,800  $\mu\text{g/g}$  of sample dissolved (3.28 wt %). This value is only 33% of the prompt gamma result and 22% of the value from the DE program. However, the flowsheet test is not designed to provide a quantitative measurement of the amount of  $Cl^-$  contained in the initial sample, and a low  $Cl^-$  value is expected due to the formation of volatile  $Cl$  containing species, such as chlorine gas ( $Cl_2$ ) and nitrosyl chloride ( $ClNO$ ), in 12 M  $HNO_3$ .<sup>[9]</sup> The  $F^-$  content (3,690  $\mu\text{g/mL}$ ) corresponds to 0.194 M and with an uncertainty of 10% corresponds to the expected value of the starting solution, 0.20 M.

The only other significant dissolved metals detected in the dissolver solution were K, Mg, Na, and Ni. The presence of K, Na, and Ni are consistent with the XRD studies performed as part of the DE Surveillance program, which detected  $NiO$ ,  $KCl$ , and  $NaCl$ . Small amounts (< 1 wt %) of several other elements were also detected including Al, barium (Ba), beryllium (Be), Ca, Cd, Cr, Cu, Fe, Mn, Sn, thorium (Th), Ti, and Zn. B and Si were excluded as their presence can be attributed to the use of a glass dissolver vessel and glass sample vials. In general, the ICP-ES data agreed with the results of the 3013 DE Surveillance Program (Table 3-2), with the exception of Al, which was significantly higher in the dissolver solution compared to the 3013 DE results. The ICP-ES values were 562% for Al, 119% for Be, 89.9% for Ca, 100% for Cr, 106% for Fe,

102% for K, 114% for Mg, 138% for Mn, 98.8% for Na, 124% for Ni, 63% for Ti, and 134% for Zn compared to the 3013 DE Surveillance values.

The sample data for the residual solids collected after the first filtration are presented in Table 3-6. The mass of insoluble residue recovered subsequent to the dissolution of Sample 10-16 was equivalent to 9.88 wt % of the starting material, with a Pu content corresponding to 5.31 – 5.95 wt % of the Pu present in the starting material. The other primary elements in the residue were W, Ta, Cr, and Ni.

**Table 3-6. Summary of Residue Data from Sample 10-16.**

Sample	Residue (wt %)	Residue (% Pu)	wt % of Initial Pu In Residue	Major Elements in the Residue
10-16	9.88	21.7 – 25.4	5.31 – 5.95	Pu, W, Ta, Cr, Ni

The dissolver solution was filtered three times. The first filtration occurred after 4 hours of dissolution and cooling of the dissolver solution to approximately 50 °C. The solution filtered readily and 0.750 g of residue was collected. The second filtration occurred 30 minutes after the addition of sufficient 2.1 M ANN solution to attain a 3:1 Al:F ratio, and the filtration was rapid, completing in 55 seconds. The solution was filtered a third time 24 hours after the addition of 2.1 M ANN and the solution filtered about 6 times slower and was complete within 6 minutes. The empirical data indicate that the ANN solubility at room temperature was likely exceeded. Similar behavior has been observed in earlier flowsheet studies.<sup>[10]</sup>

#### 4.0 Conclusions

Flowsheet testing was performed on 3013 DE Sample 10-16 using 12 M HNO<sub>3</sub> and 0.2 M KF at 108 °C for 4 hours with an initial charge of 40 g/L <sup>239</sup>Pu Eq. Sample information is listed in Table 1-2. Based on XRD analysis of the starting material (see Table 1-2), it appears that the Pu present in this material was present as PuO<sub>2</sub>. The results of the flowsheet study show that 26.1 g/L <sup>239</sup>Pu Eq. (gamma) dissolved after the first hour at temperature and that the Pu concentration remained essentially constant through 3 hours, with a slight increase in <sup>239</sup>Pu Eq. concentration at the final (4 h) time point, reaching a final <sup>239</sup>Pu Eq. concentration of 32.5 g/L (gamma) – 33.7 g/L (ICP-MS). A 4-hour dissolution time at a temperature of 108 °C and a KF concentration of 0.2 M is acceptable for performance of this flowsheet. If the target temperature cannot be reached, results of earlier tests show that dissolution at 103 °C in 12 M HNO<sub>3</sub>/0.2 M KF for 8 hours is an acceptable alternative.<sup>[11]</sup>

Prompt gamma analysis of Sample 10-16 measured 9.86 wt % Cl<sup>-</sup>, and in the DE Surveillance program, leaching studies produced 146,500 µg Cl<sup>-</sup>/g of sample (or 14.65 wt %). The sample was not washed prior to dissolution and, after 4 hours of dissolution, 2,770 µg/mL Cl<sup>-</sup> (3.28 wt %) was present in the solution. Other metallic elements detected in significant quantities included K, Mg, Na, and Ni. In general, the concentrations of all elements measured in solution were in agreement with what was expected based upon data from the 3013 DE Program (Table 1-2), with the exception of Al. The major elements present in the dissolver product solution are listed in Table 4-1. Elements attributed to the dissolution of the experimental glassware (B and Si) were omitted. A minimum concentration of 0.01 M was selected as the basis for inclusion in the table.

**Table 4-1. Elements/Anions in DE Sample 10-16 Dissolver Product Solution.**

Analyte	Be <sup>*</sup>	Ca <sup>*</sup>	Cl <sup>†</sup>	K <sup>*#</sup>	Mg <sup>*</sup>	Na <sup>*</sup>	Ni <sup>*</sup>	Pu <sup>^</sup>
Concentration (M)	0.013	0.010	0.078	0.135	0.046	0.138	0.014	0.141
Concentration (μg/g dissolved material)	1,620	5,500	34,300	72,600	15,300	43,700	11,600	469,000
<sup>*</sup> From ICP-ES data <sup>†</sup> From IC anion data <sup>#</sup> Subtracting amount attributed to starting solution (KF) <sup>^</sup> From ICP-MS data								

Upon cooling to ~50 °C, filtration of the dissolver solution occurred readily. Upon ANN addition (3 moles of Al per mole of F<sup>-</sup>) to the dissolver solution at room temperature, filtration (after a 30 minute delay) was rapid, requiring less than one minute to complete. The rate of this filtration was approximately 130 mL/min. After storage at ambient temperature 24 hours the solution filtered about 6 times slower, with filtration complete in 6 minutes. This corresponds to a rate of approximately 20 mL/min.

**Table 4-2. Flowsheet Test Summary for DE Sample 10-16.**

Flowsheet Test Conditions	12 M HNO <sub>3</sub> / 0.20 M KF for 4 h at 108 °C
Charge Ratio Tested	40 g Pu/L
Undissolved Solids (UDS)	9.88 wt %
Predominant Element in UDS	Pu
Minor Elements in UDS	W, Ta, Cr, Ni, Mg
Initial Pu in UDS	5.31 – 5.95 wt %
Gas Generation (Initial heating and first 30 min. at temperature)	~ 60 mL/g of sample
H <sub>2</sub> in Generated Gas	< 0.12 vol %



## 5.0 References

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6. Data from 3013 DE Surveillance Program, Filename "R610826-CXRD-RP1.xls" Located on SRNL Results server, August 2010.
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9. R. A. Pierce, "FY07 Year-End Report – Chloride to Nitrate Solution Conversion," WSRC-STI-2008-00104, February 2008.
10. R. A. Pierce, "Dissolution of 3013-DE Compounds: Sample 09-11," SRNL-STI-2009-00814, December 2009.
11. R. A. Pierce, "Adjustment of Dissolution Conditions to Compensate for Reduced Dissolution Temperatures", SRNL-TR-2009-00472, December 2009.

## **Appendix A**

## APPENDIX A: Sample 10-16 Solution Data

### Appendix A.1: Sample 10-16 ICP-MS Data.

Method Uncertainty = 20%

LIMS Sample #	300282327	300282328	300282329	300282330	300282710
Analyte	1 h*	2 h*	3 h*	4 h*	Fused Residue
<sup>116</sup> Sn (µg/L)	< 3.00E+04	< 3.00E+04	< 3.00E+04	< 3.00E+04	1.22E+03
<sup>118</sup> Sn (µg/L)	< 2.00E+04	< 2.00E+04	< 2.00E+04	< 2.00E+04	2.14E+03
<sup>119</sup> Sn (µg/L)	< 2.00E+04	< 2.00E+04	< 2.00E+04	< 2.00E+04	1.51E+03
<sup>120</sup> Sn (µg/L)	1.11E+05	1.17E+05	1.21E+05	1.42E+05	1.45E+04
Total Sn (g/L) †	0.339	0.359	0.371	0.436	0.0445
<sup>133</sup> Cs (µg/L)	2.72E+04	3.28E+04	3.90E+04	2.30E+04	<1.00E+03
<sup>137</sup> Ba (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	1.17E+03
<sup>138</sup> Ba (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	5.51E+03
<sup>176</sup> Hf (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	1.44E+03
<sup>177</sup> Hf (µg/L)	<4.00E+04	<4.00E+04	<4.00E+04	<4.00E+04	4.96E+03
<sup>178</sup> Hf (µg/L)	<4.00E+04	<4.00E+04	<4.00E+04	<4.00E+04	7.36E+03
<sup>179</sup> Hf (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	4.06E+03
<sup>180</sup> Hf (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	1.17E+04
<sup>181</sup> Ta (µg/L)	4.08E+04	2.24E+04	3.10E+04	<2.00E+04	3.48E+05
<sup>182</sup> W (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	1.98E+05
<sup>183</sup> W (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	1.08E+05
<sup>184</sup> W (µg/L)	<3.00E+04	<3.00E+04	<3.00E+04	<3.00E+04	2.37E+05
<sup>186</sup> W (µg/L)	<2.00E+04	<2.00E+04	<2.00E+04	<2.00E+04	2.21E+05
Total W (g/L)	<0.0979‡	<0.0979‡	<0.0979‡	<0.0979‡	0.763††
<sup>235</sup> U (µg/L)	6.06E+04	7.70E+04	7.18E+04	7.06E+04	4.38E+03
<sup>238</sup> U (µg/L)	<1.10E+05	<1.10E+05	<1.10E+05	<1.10E+05	4.02E+03
<sup>239</sup> Pu (µg/L)	2.62E+07	2.62E+07	2.66E+07	3.18E+07	2.65E+06
<sup>240</sup> Pu (µg/L)	1.54E+06	1.62E+06	1.69E+06	1.88E+06	1.73E+05
Total Pu (g/L)	27.7	27.8	28.3	33.7	2.82
% <sup>239</sup> Pu	94.4%	94.2%	94.0%	94.4%	93.9%
<sup>241</sup> Pu+ <sup>241</sup> Am (µg/L)	8.12E+04	9.04E+04	1.06E+05	1.00E+05	1.02E+04
<sup>242</sup> Pu+ <sup>242</sup> Am (µg/L)	<4.00E+04	<4.00E+04	<4.00E+04	<4.00E+04	1.12E+03
* Accounting for a dilution factor of 2. † Calculated using the natural abundance of <sup>120</sup> Sn. ‡ Calculated using the natural abundance of <sup>184</sup> W. †† Calculated using the natural abundances of all four W isotopes.					

Appendix A.2: Sample 10-16 Gamma Spectroscopy Data.

<b>LIMS Sample #</b>	<b>300282323</b>	<b>300282324</b>	<b>300282325</b>	<b>300282326</b>	<b>300282709</b>
<b>Analyte</b>	<b>1 h*</b>	<b>2 h*</b>	<b>3 h*</b>	<b>4 h*</b>	<b>Fused Residue</b>
<sup>239</sup> Pu (dpm/mL)	3.38E+09	3.32E+09	3.28E+09	4.22E+09	3.12E+08
1 Sigma % Unc.	5.00	5.27	5.00	5.00	5.00
<sup>241</sup> Am (dpm/mL)	5.06E+08	5.08E+08	5.08E+08	6.56E+08	6.04E+07
1 Sigma % Unc.	5.00	5.00	5.00	5.00	5.00
<sup>239</sup> Pu (g/L)	24.5	24.1	23.8	30.6	2.26
<sup>241</sup> Am (g/L)	0.0664	0.0667	0.0667	0.0861	0.00793
ND = not detected					
* Accounting for a dilution factor of 2.					

**Distribution:**

A. B. Barnes, 999-W  
D. A. Crowley, 773-43A  
S. D. Fink, 773-A  
B. J. Giddings, 786-5A  
C. C. Herman, 999-W  
S. L. Marra, 773-A  
A. M. Murray, 703-H  
F. M. Pennebaker, 773-42A  
G. F. Kessinger, 773-A  
R. A. Pierce, 773-A  
A. E. Visser, 773-A  
M. L. Crowder, 773-A  
S. A. Thomas, 703-46A

W. E. Harris, 704-2H  
J. B. Schaade, 704-2H  
G. J. Zachman, 225-7H  
K. J. Gallahue, 221-HBL  
K. P. Burrows, 704-2H  
J. W. Christopher, 704-2H  
A. T. Masterson, 704-2H  
M. T. Pelc, 704-2H  
T. D. Woodsmall, 704-2H  
HBLSTE, 221-HBL