Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Dissolution of Plutonium Metal Using Nitric Acid Solutions Containing Potassium Fluoride

Tracy S. Rudisill[a]; Mark L. Crowder[a]; Michael G. Bronikowski[a]
[a] Savannah River National Laboratory,, Aiken, SC, USA

To cite this Article Rudisill, Tracy S. , Crowder, Mark L. and Bronikowski, Michael G.(2008) 'Dissolution of Plutonium Metal Using Nitric Acid Solutions Containing Potassium Fluoride', Separation Science and Technology, 43: 9, 2747 — 2761

To link to this Article: DOI: 10.1080/01496390802151567

URL: http://dx.doi.org/10.1080/01496390802151567

Separation Science and Technology, 43: 2747–2761, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802151567

Dissolution of Plutonium Metal Using Nitric Acid Solutions Containing Potassium Fluoride

Tracy S. Rudisill, Mark L. Crowder, and Michael G. Bronikowski
Savannah River National Laboratory,
Aiken, SC, USA

Abstract: The deinventory and deactivation of the Department of Energy's (DOE's) FB-Line facility at the Savannah River Site (SRS) required the disposition of approximately 2000 items from the facility's vaults. Plutonium (Pu) scraps and residues which do not meet criteria for conversion to a mixed oxide fuel will be dissolved and the solution stored for subsequent disposition. Some of the items scheduled for dissolution are composite materials containing Pu and tantalum (Ta) metals. The preferred approach for handling this material is to dissolve the Pu metal, rinse the Ta metal with water to remove residual acid, and burn the Ta metal. The use of a 4 M nitric acid (HNO_3) solution containing 0.2 M potassium fluoride (KF) was initially recommended for the dissolution of approximately 500 g of Pu metal. However, prior to the use of the flowsheet in the SRS facility, a new processing plan was proposed in which the feed to the dissolver could contain up to 1250 g of Pu metal. To evaluate the use of a larger batch size and subsequent issues associated with the precipitation of plutonium-containing solids from the dissolving solution, scaled experiments were performed using Pu metal and samples of the composite material.

In the initial experiment, incomplete dissolution of a Pu metal sample demonstrated that a 1250 g batch size was not feasible in the HB-Line dissolver. Approximately 45% of the Pu was solubilized in 4 h. The remaining Pu metal was converted to plutonium oxide (PuO_2). Based on this work, the dissolution of 500 g of Pu metal using a 4–6 h cycle time was recommended for the HB-Line facility. Three dissolution experiments were subsequently performed using samples of the Pu/Ta composite material to demonstrate conditions which reduced the risk of precipitating a double fluoride salt containing Pu and K from the dissolving solution. In these experiments, the KF concentration was reduced from 0.2 M to either 0.15 or 0.175 M. With the use of 4 M HNO_3 and a reduction in the KF concentration to 0.175 M, the dissolution of 300 g of Pu metal is expected

Received 22 October 2007; accepted 29 March 2008.

Address correspondence to Tracy S. Rudisill, Savannah River National Laboratory, Aiken, SC 29808, USA. E-mail: tracy.rudisill@srnl.doe.gov

to be essentially complete in 6 h. The dissolution of larger batch sizes would result in the formation of PuO_2 solids. Incomplete dissolution of the PuO_2 formed from the metal is not a solubility limitation, but can be attributed to a combination of reduced acidity and complexation of fluoride which slows the dissolution kinetics and effectively limits the mass of Pu dissolved.

Keywords: Dissolution, nitric acid, plutonium metal

INTRODUCTION

Scrap materials containing Pu metal are currently being dissolved in Phase I of the DOE's HB-Line facility at the SRS as part of a program to disposition nuclear materials from the deactivation of several vaults in the site's FB-Line facility. Some of the materials scheduled for disposition are composite materials containing Pu and Ta metals. Since Ta metal is essentially insoluble in HNO_3/fluoride solutions, the preferred approach for handling this material is to dissolve the Pu metal, rinse the Ta metal with process water to remove the residual acid, and then burn the Ta metal.

The dissolution of Pu metal using a HNO_3/fluoride flowsheet was initially investigated at the DOE's Rocky Flats Plant. Miner et al. performed a series of experiments in which unalloyed (alpha phase) Pu metal was dissolved in solutions containing 1–5 M HNO_3 and 0.01–0.13 M hydrofluoric acid (HF) at 26–69°C (1). The maximum rate of dissolution occurred at approximately 3 M HNO_3 in combination with an HF concentration of 0.13 M (the highest investigated) at any temperature between 26 and 69°C. Additional dissolution experiments with alpha and delta-stabilized metal were performed by Holcomb at the SRS (2–3). The focus of these experiments was the effect of the concentration of aluminum (Al^{3+}) on the dissolution rate. The experiments verified the optimal flowsheet recommended by Miner et al. and demonstrated that the dissolution rate was sensitive to the presence of Al^{3+} and other elements which complex fluoride.

The complexation of fluoride decreases its activity in solution and effectiveness as a catalyst for the dissolution of PuO_2. The dissolution of both alpha and delta-stabilized metal in HNO_3 requires a small amount of free fluoride to inhibit the formation of a PuO_2 layer on the surface of the metal due to oxidation by HNO_3. Generally, the rate of dissolution increases with the fluoride concentration and is only constrained by plutonium tetrafluoride precipitation. The HNO_3 concentration must also remain dilute to reduce the surface oxidation rate. This requirement is even more important for delta-stabilized metal. Karraker reported that the surface of delta-stabilized Pu metal was much more reactive toward oxidation by nitrate than that of alpha phase metal (4).

To dissolve the Pu/Ta composite materials, the use of a 4 M HNO_3 solution containing 0.2 M KF at 70°C for 10 h followed by 4 h at 95°C was initially recommended for a batch size of approximately 500 g of Pu metal (5). However, prior to the use of the flowsheet, a new processing plan was proposed in which the feed to the HB-Line dissolver could contain up to 1250 g of Pu metal. Due to the potential increase in the mass of Pu, the use of the existing flowsheet in the facility was not recommended without a scaled laboratory demonstration. A fluoride concentration of 0.2 M was likely insufficient to dissolve the desired amount of Pu metal which would result in the generation of undissolved PuO_2. In a scaled experiment based on the dissolution of 500 g of metal in a 15 L dissolver, Rudisill et al. (6) only dissolved about 90% of the Pu using a 4 M HNO_3/0.1 M KF solution at 80°C. The remaining Pu was collected as undissolved PuO_2. A steady decrease in the dissolution rate during the experiment was attributed to the complexation of fluoride by the dissolved Pu.

To determine the feasibility of dissolving larger batches of the composite material, a scaled experiment was performed in which Pu metal was dissolved using a 4 M HNO_3 solution containing 0.2 M KF at 95°C. Tantalum metal was treated as an inert material and was not used in the experiment. Based on this work, the dissolution of approximately 500 g of Pu metal using a 4–6 h cycle time was recommended for the HB-Line dissolver (7). However, during the initial dissolution campaign, the total amount of Pu and Ta in the dissolver charge was limited to nominally 300 g based on nuclear safety constraints. The smaller mass of Pu (which increased the fluoride to Pu ratio) coupled with significant evaporation of solution during several dissolver runs resulted in the precipitation of a double fluoride salt of K and Pu (KPu_2F_9). Dissolution of the salt in the HB-Line dissolver required the addition of aluminum nitrate and subsequent heating for 4 h, a lengthy and undesired processing step. As a result of these processing difficulties, three optimization experiments were performed at lower KF concentrations using samples of the composite material to demonstrate conditions which reduced the risk of precipitating solids.

The experimental methods used to develop the initial Pu/Ta dissolution flowsheet and to perform the optimization experiments are described in the follow section. In subsequent sections, results and conclusions including flowsheet recommendations from both experimental programs are presented and discussed.

EXPERIMENTAL

Development of Pu/Ta Dissolution Flowsheet

A scaled dissolution experiment was performed in which 6.7 g of Pu metal were dissolved in 80.5 mL of a 4 M HNO_3 solution containing 0.2 M KF at 95°C. The experiment simulated the dissolution of a composite

Table 1. Comparison of Pu flowsheet demonstration with HB-line

Flowsheet	Solution	Dissolver volume (L)	Pu mass (g)	Pu[a] conc. (g/L)	Pu[a] conc. (M)
HB-Line	4 M HNO_3/0.2 M KF	15	1250	83.3	0.35
Demonstration	4 M HNO_3/0.2 M KF	0.0805	6.70	83.2	0.35

[a] Assumes complete dissolution.

material containing Pu and Ta metals at nominally 1/200th scale. A comparison of the proposed HB-Line flowsheet and the laboratory demonstration is shown in Table 1.

To perform the flowsheet demonstration, 80.5 mL of solution were added to a 250 mL glass dissolver fitted with a water-cooled condenser. The vessel was heated and stirred using a hot plate equipped with a magnetic stirrer. A thermocouple probe connected to the hot plate was used for temperature control. The temperature of the dissolving solution was held at 95°C for 8 h. Solution samples were taken after 4 and 8 h. After the initial 8 h of heating, additional KF was added to the dissolving solution to increase the concentration to 0.3 M. The solution was then heated for an additional 8 h at 95°C to determine the effect of the higher fluoride concentration. Solution samples were taken 4 and 8 h after the increase to 0.3 M KF.

During the flowsheet demonstration, the volume of the offgas generated during the dissolution and the hydrogen (H_2) concentration were measured. To sample and collect the offgas, the outlet from the condenser was connected with plastic tubing to 25 mL sample bulbs and 1 L Tedlar® bags. The sample bulbs were fabricated with glass stopcocks on the ends to provide a means to isolate the sample. Quick disconnects (which sealed upon disconnection) were used to attach and remove the sample bulbs and Tedlar® bags from the plastic tubing. The total volume of gas generated during the dissolution was collected. The gas samples bulbs and Tedlar® bags were simultaneously removed and replaced. The volume of gas collected during the dissolution was determined by the difference in the amount of water displaced by the empty (evacuated) and filled bags. Gas analyses were performed by gas chromatography (GC). The ^{239}Pu concentration in the samples was measured by gamma pulse height analysis (GPHA). The total Pu concentration was calculated by assuming the metal was weapons grade material (i.e., 94 wt % ^{239}Pu and 6 wt % ^{240}Pu).

Flowsheet Optimization Experiments

Three dissolution experiments were performed using samples of the Pu/Ta composite material to demonstrate conditions which reduced

Table 2. Comparison of conditions for dissolution of Pu/Ta composite materials

	Dissolving solution			Charge/sample mass	
Flowsheet	HNO_3 (M)	KF (M)	Liquid volume (L)	Total (g)	Pu (g)
HB-Line	4	0.20	15	500	500
Exp. 1	4	0.15	0.210	9.04	7.08[a]
Exp. 2	4	0.175	0.194	8.33	7.08[a]
Exp. 3	4	0.175	0.580	24.99	14.15[a]

[a] Estimated mass of Pu.

the risk of precipitating Pu-containing solids in the HB-Line dissolver. The solid-to-liquid ratio for the first experiment was based on the initial flowsheet development (i.e., dissolution of 500 g of Pu metal in the 15 L dissolver). The volume of solution used in the experiment was determined by assuming the HB-Line charge was 100% Pu metal and using the estimated Pu mass of the sample to scale the HB-Line dissolver volume. In the subsequent experiments, the same total sample mass-to-liquid ratio was maintained, although the fluoride concentration of the solution was increased in Experiments 2 and 3 from 0.15 to 0.175 M. Table 2 provides a comparison of the initial HB-Line flowsheet and the conditions used in the optimization experiment.

Experiments 1 and 2 were performed with the same equipment used to demonstrate the initial dissolution flowsheet. In Experiment 3, the larger solution volume required the use of a 1 L round-bottom flask as the dissolver. The solution was heated and stirred using a heating mantle equipped with a magnetic stirrer. A water-cooled condenser was used to reduce evaporation losses. The temperature was manually controlled by observing a calibrated thermometer and adjusting the set point of the heating mantle. In each experiment, the temperature of the dissolving solution was maintained at 90–100°C for 5–6 h. Solution samples were periodically removed from the dissolver. The solution was also sampled following termination of each dissolution. In Experiments 1 and 3, it was necessary to dissolve a small amount of Pu metal which was not completely removed from the Ta metal during the initial dissolution as well as solids recovered from the solution. The dissolution of these materials is discussed in the following section.

During each experiment, the volume of offgas was measured and samples collected for H_2 analysis. The offgas collection and sampling procedure was the same as used to demonstrate the initial dissolution flowsheet. Gas analyses were performed by GC. The Pu concentrations were calculated from the results of a GPHA assuming the Pu was weapons grade material.

RESULTS AND DISCUSSION

Development of Pu/Ta Dissolution Flowsheet

When the Pu metal sample was added to the dissolving solution, fine brown solids, presumably PuO_2, were removed from the metal surface and suspended in the solution. During the initial heating, the solution appeared gray to light green and gradually darkened to an olive green. After 4 h at nominally 95°C, liquid and gas samples were taken and a larger stir bar was added in an attempt to suspend solids which were collecting on the bottom of the flask. Following 8 h at temperature and overnight cooling, the fluoride concentration was increased to 0.3 M by the addition of a 2.1 mL aliquot of 3.8 M KF. Upon further heating at 95°C, the solution remained olive green with tan solids on the bottom of the dissolving flask. After liquid and gas samples were removed following 4 h of heating (12 h cumulative), the stir rate was increased from 200 to 800 rpm and all solids were eventually suspended. The solution was then heated for an additional 4 h (16 h cumulative) at 95°C and liquid and gas samples were collected.

The volume of the dissolving solution was measured by decanting the solution from the residual solids. The volume was 71 mL, indicating evaporative losses of about 7 mL; a total of 2.4 mL of the solution was removed as liquid samples. The solution and solids were then recombined and a 10 mL aliquot of concentrated (15.7 M) HNO_3 was added to raise the total acid concentration to approximately 6 M. The solution was heated for an additional 2 h at 90–96°C. Because of the darkness of the solution, no visual changes were observed. During filtration of the dissolving solution, the filter assembly leaked resulting in a loss of a portion of both solution and solids. The solids, which were recovered, dissolved easily in an 8 M HNO_3 solution containing 0.2 M KF when heated to 95–100°C for approximately 3 h.

The solution analyses for the Pu metal dissolution experiment are summarized in Table 3. The one sigma uncertainties associated with the analyses are ± 5–10%. To calculate the amount of Pu metal which was solubilized as a function of time, the volume of solution at each sample time was estimated using the initial volume of solution, the volume of samples removed, the volume of 3.8 M KF added following 8 h of heating, and the measured volume (71 mL) following 16 h of cumulative heating. The calculation assumed uniform evaporative losses during the 16 h of heating. The measured Pu concentration and estimated volume were then used to calculate the mass of Pu in solution. The calculated mass is expressed as a percentage of the initial sample mass in Table 3. The mass of Pu solubilized as a function of time shows that nominally 45% of the total Pu dissolved during the first 4 h of heating. The remaining Pu metal was converted to PuO_2. The concentrations of

Table 3. Solution analyses for Pu metal dissolution

Sample No.	Fluoride (M)	Cumulative Time (h)	Pu Conc. (g/L)	Estimated Volume (mL)	Pu Solubilized (%)
1	0.2	4	38.7	78.2	45
2	0.2	8	38.4	75.5	43
3	0.3	12	32.0	74.5	36
4	0.3	16	27.9	71.8	30
5	0.3[a]	18	46.5	79.8	55

[a] Total acid increased from 4 m to approximately 6 M.

Pu in the dissolving solution were essentially identical at 4 and 8 h indicating that a cycle time longer than about 4 h did not result in the solubilization of additional material. When additional KF was added and the solution heated for 8 h, the soluble Pu decreased by 33%. The decrease in concentration was attributed to the precipitation of a double fluoride salt of K and Pu (KPu_2F_9). The precipitation of the double salt was observed in a 27 g/L Pu solution containing a total fluoride concentration between 0.26 and 0.28 M during previous flowsheet development activities (8). Incomplete dissolution of the PuO_2 formed from the metal is not a solubility limitation. Plutonium oxide has been successfully dissolved using 12–14 M HNO_3 containing 0.1–0.2 M fluoride to concentrations which greatly exceed 100 g/L (9–10). A combination of low acidity and complexation of fluoride by the soluble Pu slowed the dissolution kinetics of the PuO_2 and effectively limited the mass of Pu which was dissolved.

The addition of a 10 mL aliquot of 15.7 M HNO_3 to the solution with 2 h of heating resulted in a significant increase in the amount of Pu dissolved. The increase in concentration was attributed to the partial dissolution of the double salt and the PuO_2. The addition of the acid resulted in a 14% increase in volume which likely solubilized some of the KPu_2F_9. An increase in the acid concentration also increases the rate at which PuO_2 dissolves. Therefore, an increase in the total acid concentration to approximately 6 M was expected to increase the amount of PuO_2 which readily dissolved with additional heating.

Flowsheet Optimization Experiments

Experiment 1

Since data were available from Pu metal dissolutions performed using 4 M HNO_3 solutions containing 0.1 and 0.2 M fluoride (6–7), a KF concentration of 0.15 M was selected for the initial optimization experiment. When the Pu/Ta composite material was added to the dissolving solution, the formation of a blue color characteristic of a Pu^{3+} nitrate solution was initially observed. Subsequently, the solution turned brown as the Pu oxidized to Pu^{4+}. Throughout the dissolution, the sample generated small bubbles of gas. The bubbles originated from the bottom of the sample which indicated the Pu metal side of the material faced downward and was in contact with the bottom of the vessel. The orientation of the sample may have reduced the rate at which the Pu metal dissolved. The presence of nitrogen dioxide (NO_2) gas in the sample bulbs and Tedlar^{TM} bags was confirmed by the brown color. Prior to removing the first gas sample, a small leak at the ground glass joint between the dissolving vessel and condenser was observed and corrected; therefore, the volume of gas collected and the composition of the first gas sample were not completely representative of this dissolution period.

Some difficulty in heating the solution to the desired temperature was encountered due to a poor thermocouple connection at the hot plate; however, the solution was still heated for approximately 5 h at a temperature between 85 and 95°C. When the experiment was terminated and the remaining sample was inspected, it was apparent that the Pu metal did not completely dissolve. To dissolve the remaining Pu metal, the sample was subsequently placed in approximately 35 mL of an 8 M HNO_3 solution containing 0.15 M KF. Complete dissolution of the remaining Pu metal required approximately 2.5 h. It was also necessary to dissolve a small amount of PuO_2 solids recovered from the original solution. The solids were isolated by filtration and dissolved using approximately 70 mL of a solution containing 8 M HNO_3/0.15 M KF. The PuO_2 required less than 1 h for complete dissolution.

The Pu solution analyses for Experiment 1 are summarized in Table 4. The one sigma uncertainties associated with the analyses are ±5–10%. To calculate the amount of Pu metal dissolved as a function of time, the volume of solution at each sample time was estimated using the initial volume of solution, the volume of samples removed, and the

Table 4. Pu solution analyses for experiment 1

Sample no.	Cumulative time (h)	Pu concentration (g/L)	Estimated volume (mL)	Pu dissolved (%)	HB-line basis (g)
1	2.08	13.7	210.0	57.5	206
2	4.08	17.7	209.5	73.8	265
3	6.08	22.9	209.0	95.5	343

measured volume following termination of the experiment. The volume of solution evaporated during the experiment was insignificant. The measured Pu concentration and estimated volume were used to calculate the mass of Pu in solution. The calculated mass is expressed as a percentage of the total mass of Pu dissolved which includes the initial Pu metal, residual Pu metal, and the PuO_2 solids. The mass of Pu dissolved as a function of time shows that >95% of the total Pu dissolved during the 6.08 h dissolution cycle. It should be noted that the solution was only heated to a temperature greater than 85°C for approximately 5 h due to problems with the hot plate thermocouple. Table 4 also provides an estimate of the mass of Pu which would dissolve in the HB-Line dissolver using the solution volume to scale the mass of Pu dissolved during the experiment. The mass of Pu dissolved in 6.08 h (4.79 g) scales to the dissolution of 343 g of Pu in the HB-Line dissolver.

It is likely that the Pu metal remaining on the Ta substrate would have dissolved if the dissolution time had been extended. This assumption is based on the steady increase in the Pu concentration observed during the last several hours of the dissolution experiment (Fig. 1). It is doubtful that the PuO_2 formed during the dissolution would have dissolved. As noted above, incomplete dissolution of the PuO_2 is not a solubility limitation. A combination of low acidity and complexation of fluoride by the

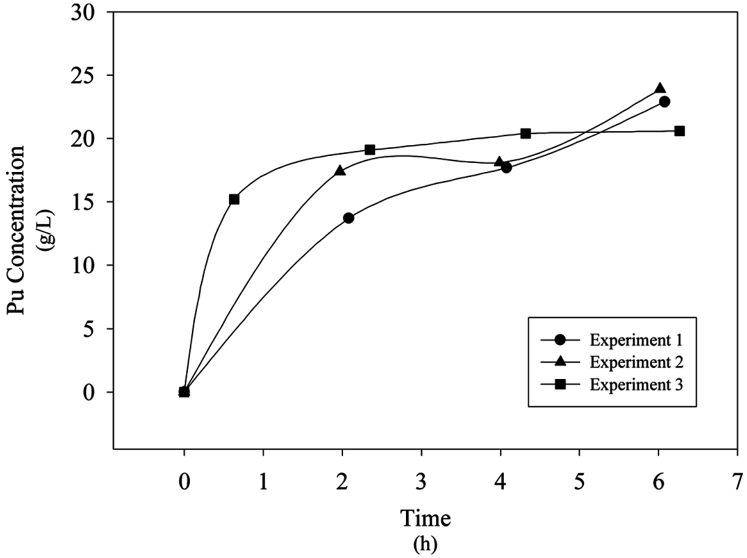

Figure 1. Dissolution of composite materials containing Pu and Ta metals.

soluble Pu slowed the dissolution kinetics of the PuO_2 and effectively limited the mass which dissolved.

Experiment 2

Since complete dissolution of the Pu metal associated with the composite material was not achieved in Experiment 1, the fluoride concentration was increased to 0.175 M. The higher fluoride concentration increases the rate of Pu metal dissolution. The sample mass-to-liquid volume ratio used in this experiment was maintained at the same value as used in Experiment 1. During the dissolution, essentially the same behavior as seen in the initial experiment was observed. The solution originally turned a blue color which transitioned to brown as Pu^{3+} oxidized to Pu^{4+}. Small bubbles of gas were generated at the top surface of the metal indicating that the Pu metal side of the material was face-up in this experiment based on the origination of the bubbles. The presence of NO_2 in the offgas was evident based on the brown color of the gas in the sample bulbs and Tedlar^{TM} bags. Following approximately 6 h at a temperature of 90–100°C, the sample was removed from the dissolver and inspected. Based on the visual observation, it was clear that the Pu metal had completely dissolved and the experiment was terminated. No solids were observed when the solution was filtered following the dissolution.

The Pu solution analyses for Experiment 2 are summarized in Table 5. The one sigma uncertainties associated with the analyses are ± 5–10%. To calculate the amount of Pu metal dissolved as a function of time, the same procedure as used in Experiment 1 was followed. The volume of solution evaporated during the experiment was estimated at 10.0 mL. A constant evaporation rate was assumed. The measured Pu concentration and estimated volume were then used to calculate the mass of Pu in solution. The calculated mass is expressed as a percentage of the total mass of Pu dissolved in Table 5. Complete dissolution of the Pu

Table 5. Pu solution analyses for experiment 2

Sample No.	Cumulative Time (h)	Pu Concentration (g/L)	Estimated Volume (mL)	Pu Dissolved (%)	HB-Line Basis (g)
1	1.97	17.4	190.7	76.0	261
2	3.99	18.0	186.9	77.1	271
3	6.02	23.9	183.0	100.0	358

metal was achieved in 6.02 h. Table 5 also provides an estimate of the mass of Pu which would be dissolved in the HB-Line dissolver using the solution volume to scale the mass of Pu dissolved during the experiment. The mass of Pu dissolved in 6.02 h (4.37 g) scales to the dissolution of 358 g of Pu in the HB-Line dissolver.

Experiment 3

Experiment 3 was designed as a duplication of the second experiment except that it was performed at a larger scale. Visual observations during the dissolution were generally the same as in the previous two experiments. Following approximately 6 h of heating at 95–100°C, the remains of the Pu/Ta sample were removed from the vessel for inspection. It appeared that the Pu metal had dissolved; however, a bead of material which was thought to be part of a weld was observed on the surface of the Ta metal. The experiment was terminated based on this interpretation, but a decision was made to continue the dissolution at a later date to ensure that the Pu metal had completely dissolved.

The Ta metal substrate was subsequently leached using approximately 125 mL of a 4 M HNO_3 solution containing 0.175 M KF. When placed in the solution, it was apparent that the sample still contained Pu metal. Small gas bubbles were generated at the metal surface and the solution color transitioned from blue to brown. After heating the solution for 3.5 h at 95–100°C, the metal completely dissolved. Both sides of the Ta substrate were clean. It was also necessary to dissolve a small amount of PuO_2 solids recovered from the original dissolving solution. The solution was filtered and solids were dissolved in 100 mL of an 8 M HNO_3/0.15 M KF solution. The solids easily dissolved in less than 1 h when heated to 90°C.

The Pu solution analyses for Experiment 3 are summarized in Table 6. The one sigma uncertainties associated with the analyses are ± 5–10%. To calculate the amount of Pu metal dissolved as a function of time, the same procedure as used in Experiments 1 and 2 was followed. The volume of solution evaporated during the experiment was estimated at 15.5 mL. A constant evaporation rate was assumed to estimate the solution volumes. The measured Pu concentration and estimated volume were then used to calculate the mass of Pu in solution. The mass of Pu dissolved as a function of time shows that >92% of the total Pu dissolved during the 6.27 h dissolution cycle which scales to the dissolution of 309 g of Pu in the HB-Line dissolver.

The data in Table 6 show that the rate of Pu metal dissolution in Experiment 3 slowed significantly beyond approximately 4 h. This fact is

Table 6. Pu solution analyses for experiment 3

Sample no.	Cumulative time (h)	Pu concentration (g/L)	Estimated volume (mL)	Pu dissolved (%)	HB-line basis (g)
1	0.63	15.2	578.4	70.3	228
2	2.35	19.1	573.7	87.8	287
3	4.32	20.4	568.3	92.6	305
4	6.27	20.6	563.0	92.7	309

also illustrated on Fig. 1. The Pu concentration appears to have reached a constant value. The slow rate of dissolution, at least in part, could be attributed to the diminishing surface area of the small bead of Pu remaining on the Ta surface. The reduction in the fluoride activity due to complexation with Pu also contributed to the reduction in the rate of dissolution. When fresh solution was used to dissolve the remaining metal, the dissolution proceeded at a significantly higher rate. Given time (much >4 h), the Pu metal may have dissolved using the original solution or a significant portion of the metal may have oxidized to PuO_2. If the metal oxidized to PuO_2, it is likely that little of the material would have dissolved due to the fluoride complexation and the low HNO_3 concentration.

Offgas Analysis

The H_2 concentration in the offgas samples from the development of the Pu/Ta dissolution flowsheet and the optimization experiments was at or below the detection limit (0.1 vol %) of the GC used for the analyses. These results are somewhat surprising since the dissolution of Pu metal proceeds by acid (equation 1) as well as oxidation by nitrate (equation 2–4) (6).

$$Pu + 4HNO_3 \rightarrow Pu(NO_3)_4 + 2H_2 \qquad (1)$$

$$Pu + 8HNO_3 \rightarrow Pu(NO_3)_4 + 4NO_2 + 4H_2O \qquad (2)$$

$$3Pu + 16HNO_3 \rightarrow 3Pu(NO_3)_4 + 4NO + 8H_2O \qquad (3)$$

$$2Pu + 10HNO_3 \rightarrow 2Pu(NO_3)_4 + 2N_2O + 5H_2O \qquad (4)$$

Throughout most of the dissolutions, brown gas was observed in the headspace of the dissolver vessel, sample bulbs, and in the Tedlar^{TM} bags. The brown color is indicative of NO_2, which was not detectable by the

Table 7. Offgas generation during the dissolution of plutonium metal

Activity	Material	Concentrations		Offgas generation
		HNO_3 (M)	KF (M)	(mole/mole Pu)
Flowsheet Dev.	Pu Metal	4–6	0.2–0.3	1.2
Experiment 1	Pu/Ta Composite	4	0.15	0.31
Experiment 2	Pu/Ta Composite	4	0.175	0.83
Experiment 3	Pu/Ta Composite	4	0.175	0.87

GC used for these analyses. The dissolution of Pu metal by acid oxidation is maximized at low dissolution temperatures. The presence of NO_2 gas, an indication of oxidation by nitrate, was generally not observed below approximately 70°C.

Small amounts of H_2 have been measured during the dissolution of Pu metal in HNO_3/fluoride systems. Rudisill et al. (6) measured a H_2 concentration of 2.6 vol% in a gas sample collected during the dissolution of Pu metal using a 4 M HNO_3 solution containing 0.1 M KF. However, prior to adjusting the concentration for dilution by the gas originally in the dissolving system used in that study, the measured concentration was only 0.47 vol%. Miner et al. (1) reported that gas samples withdrawn from just above the surface of nitric/hydrofluoric acid solutions used to dissolve alpha phase Pu metal always contained ≤ 0.3 vol% H_2. Therefore, small concentrations of H_2 produced during the dissolution experiments could have easily been diluted below the detection limit of the GC.

The total amounts of gas generated during the development of the Pu/Ta dissolution flowsheet and the subsequent three optimization experiments are summarized in Table 7. The low gas generation measured in Experiment 1 can be attributed, to the leak which occurred in the dissolving system during the early part of the dissolution when the majority of the offgas was generated. The higher value measured during the development of the initial flowsheet compared to Experiments 2 and 3 is likely attributed to differences in the composition of the solutions which affect the dissolution mechanisms and the composition of the gases produced.

CONCLUSIONS

A scaled laboratory experiment demonstrated that complete dissolution of 1250 g of Pu metal using a 4 M HNO_3 solution containing 0.2 M KF at 95°C is not feasible in the HB-line dissolver. Analytical results from the experiment showed that nominally 45% of the Pu was solubilized in 4 h. The remaining Pu metal was converted to PuO_2. The concentrations of Pu in the dissolving solution were essentially identical at 4 and 8 h, indicating that a cycle time longer than about 4 h did not result in the dissolution of additional Pu. When the fluoride concentration was increased to approximately 0.3 M, the soluble Pu decreased by 33%. The decrease in the amount of soluble Pu was due to the precipitation of a double fluoride salt of K and Pu from the dissolving solution. Incomplete dissolution of the PuO_2 formed from the metal is not a Pu solubility limitation, but can be attributed to a combination of reduced acidity and complexation of fluoride which slowed the dissolution kinetics and effectively limited the mass of Pu which was dissolved. Based on this work, the dissolution of approximately 500 g of Pu metal using a 4–6 h cycle time was recommended for the HB-Line dissolver.

In subsequent experiments, the use of lower KF concentrations was investigated to reduce the risk of precipitating Pu-containing solids in the HB-Line dissolver. When 0.15 M KF was used in the dissolving solution, $>95\%$ of the Pu metal dissolved in approximately 6 h. The remaining Pu was present as a small amount of Pu metal and PuO_2 solids. In the initial experiment with 0.175 M KF, complete dissolution of the Pu metal was achieved in 6 h. The second experiment using 0.175 M KF was prematurely terminated after approximately 6 h following the dissolution of $>92\%$ of the Pu; however, the dissolution of additional Pu was severely limited due to the slow rate observed beyond approximately 4 h. The slow rate of dissolution, at least in part, could be attributed to the diminishing surface area of the remaining Pu metal. A small amount of PuO_2 solids were also present in the solution. Based on these experiments, the dissolution of 300 g of Pu metal using a 4 M HNO_3 solution containing 0.175 M KF was recommended for the HB-Line dissolver. A dissolution temperature of nominally 95°C should allow for essentially complete dissolution of the metal in 6 h.

The H_2 concentration in the offgas samples from the dissolution of both the Pu metal and Pu/Ta composite material was at or below the detection limit (0.1 vol%) of the GC used for the analyses. These results were somewhat surprising since the dissolution of Pu metal proceeds by acid oxidation (which generates H_2) as well as nitrate oxidation. The measured concentrations of H_2 in the offgas from Pu metal dissolutions in previous investigations were <0.5 vol % (1,6); therefore, small concentrations produced during the dissolution experiments could have easily been diluted below the detection limit of the GC.

REFERENCES

1. Miner, F.J.; Nairn, J. H.; Berry, J.W. (1969) Dissolution of plutonium in dilute nitric acid. *I&EC Product Research and Development*, *9*: 402–405.
2. Holcomb, H.P. (1989) *Dissolving Alpha-Phase Plutonium Metal*, Report WSRC-RP-89–00616, Westinghouse Savannah River Company, Aiken, SC.
3. Holcomb, H.P. (1990) *Laboratory-Scale Dissolution of Delta-Phase Plutonium Metal*, Report WSRC-TR-90–0101, Westinghouse Savannah River Company, Aiken, SC.
4. Karraker, D.G. (1983) *Dissolution of Plutonium Metal in* HNO_3-N_2H_4-*KF*, Report DP-1666, E. I. du Pont de Nemours & Co., Aiken, SC.
5. Bronikowski, M.G.; Scogin, J.H.; Pierce, R.A. (March 2005) *Vanadium and Tantalum Disposition for HB-Line*, Report WSRC-TR-2005–00134, Westinghouse Savannah River Company, Aiken, SC.
6. Rudisill, T.S.; Crowder, M.L. (2006) Dissolution of Fissile Materials Containing Plutonium and Beryllium Metals. *Sep. Sci. Technol.*, *41*: 2013–2029.
7. Rudisill, T.S.; Crowder, M.L.; Bronikowski, M.G. (May 2006) *Dissolution of Fissile Materials Containing Vanadium and Tantalum Metals*, WSRC-TR-2006–00159, Washington Savannah River Company, Aiken, SC.
8. Laurinat, J.E.; Crowder, M.L.; Kessinger, G.F. (May 2005) *Information on the Solubility of Plutonium in Nitric Acid/Fluoride Solutions*, Report SRNL-ATS-2005–00031, Rev.1, Westinghouse Savannah River Company, Aiken, SC.
9. Burney, G.A. (October 1984) *Dissolution of Rocky Flats Foundry* PuO_2, Report DPST-84–782, E. I. du Pont de Nemours & Co., Aiken, SC.
10. Molen, G.F. (1967) *Dissolution of Plutonium Oxide*, Report RFP-922, The Dow Chemical Company, Golden, CO.