Solubility of Plutonium (IV) Oxalate During Americium/Curium Pretreatment

by

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June 1999

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Solubility of Plutonium (IV) Oxalate During Americium/Curium Pretreatment

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Summary

Approximately 15,000 L of solution containing isotopes of americium and curium (Am/Cm) will undergo stabilization by vitrification at the Savannah River Site (SRS). Prior to vitrification, an in-tank pretreatment will be used to remove metal impurities from the solution using an oxalate precipitation process. Material balance calculations for this process, based on solubility data in pure nitric acid, predict approximately 80% of the plutonium in the solution will be lost to waste. Due to the uncertainty associated with the plutonium losses during processing, solubility experiments were performed to measure the recovery of plutonium during pretreatment and a subsequent precipitation process to prepare a slurry feed for a batch melter. A good estimate of the plutonium content of the glass is required for planning the shipment of the vitrified Am/Cm product to Oak Ridge National Laboratory (ORNL).

The plutonium solubility in the oxalate precipitation supernate during pretreatment was 10 $\mu\text{g/mL}$ at 35°C. In two subsequent washes with a 0.25M oxalic acid/0.5M nitric acid solution, the solubility dropped to less than 5 $\mu\text{g/mL}$. During the precipitation and washing steps, lanthanide fission products in the solution were mostly insoluble. Uranium, and alkali, alkaline earth, and transition metal impurities were soluble as expected. An elemental material balance for plutonium showed that greater than 94% of the plutonium was recovered in the dissolved precipitate. The recovery of the lanthanide elements was generally 94% or higher except for the more soluble lanthanum. The recovery of soluble metal impurities from the precipitate slurry ranged from 15 to 22%. Theoretically, 16% of the soluble oxalates should have been present in the dissolved slurry based on the dilution effects and volumes of supernate and wash solutions removed. A trace level material balance showed greater than 97% recovery of americium-241 (from the beta decay of plutonium-241) in the dissolved precipitate, a value consistent with the recovery of europium, the americium surrogate.

In a subsequent experiment, the plutonium solubility following an oxalate precipitation to simulate the preparation of a slurry feed for a batch melter was 21 $\mu\text{g/mL}$ at 35°C. The increase in solubility compared to the value measured during the pretreatment experiment was attributed to the increased nitrate concentration and ensuing increase in plutonium complexation. The solubility of the plutonium following a precipitant wash with 0.1M oxalic acid was unchanged. The recovery of plutonium from the precipitate slurry was greater than 97% allowing an

estimation that approximately 92% of the plutonium in Tank 17.1 will report to the glass. The behavior of the lanthanides and soluble metal impurities was consistent with the behavior seen during the pretreatment experiment. A trace level material balance showed that 99.9% of the americium was recovered from the precipitate slurry. The overall recovery of americium from the pretreatment and feed preparation processes was greater than 97%, which was consistent with the measured recovery of the europium surrogate.

Introduction

Approximately 15,000 L of solution containing isotopes of Am/Cm are currently stored in F-Canyon Tank 17.1 at the SRS. These isotopes were recovered during plutonium-242 production campaigns in the mid and late 1970's. The continued storage of this solution was identified as an item of urgent concern in the Defense Nuclear Facility Safety Board's Recommendation 94-1.[1] To address this concern, SRS is planning to stabilize the Am/Cm in a strontium aluminoborosilicate glass. The Multi-Purpose Processing Facility (MPPF) in F-Canyon will be used for the vitrification process. Pretreatment operations will be performed in canyon vessels to separate the actinides and lanthanides from alkali, alkaline earth, and transition metal impurities prior to vitrification.

The pretreatment operations for the Am/Cm program include adjusting the nitric acid concentration of the solution to less than 1M, precipitating the actinides and lanthanides as oxalates, washing the soluble metallic impurities from the precipitate slurry, solubilizing the precipitate, and concentrating the solution prior to vitrification (see Figure 1). Material balances performed for these operations predict that approximately 80% of the plutonium in the Am/Cm solution will be lost to waste streams during the pretreatment operations. This value was calculated based on the solubility of plutonium (IV) oxalate in 1M nitric acid solution.[2] The coprecipitation effects of other actinides and the lanthanides were ignored.

Due to the uncertainty associated with the plutonium losses during the pretreatment operations, solubility experiments were performed to measure the recovery during this process. A good estimate of the plutonium recovery is required for planning the shipment of the vitrified Am/Cm product to ORNL. The actual recovery of plutonium could potentially impact the glass inventory in a shipping cask due to limitations on the total curies of plutonium. If the shipping cask contains less than 20 curies of plutonium, the shipment is exempt from most packaging and transportation requirements specified in the Code of Federal Regulations which are normally associated with fissile material.[3]

An additional solubility experiment was also performed to support the Am/Cm vitrification flowsheet under development for an induction heated, cylindrical melter. The batch flowsheet being developed for this melter utilizes an oxalate slurry as the feed. Following concentration of the Am/Cm solution, the feed to the vitrification process is denitrated with formic acid to adjust the nitric acid concentration to less than 1M. Small volumes of solution (25 liters) are transferred to the MPPF and an oxalate precipitation performed using the amount of solution (approximately 7 liters) required to fabricate a single can of glass. The precipitation is performed using nominally 0.9M oxalic acid, an excess oxalate concentration of 0.3M, a digestion period of 30 min, and a single wash using 0.1M oxalic acid. To simulate the feed preparation process, a simulated Am/Cm solution was prepared based on the pretreatment material balance and plutonium solubility data from the simulated pretreatment experiment. An oxalate precipitation was then performed using the same conditions proposed for the batch flowsheet. Samples of the precipitation supernate and wash solution were analyzed to determine the solubility of plutonium and other elements of interest.

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Am/Cm Pretreatment

Experimental

A laboratory-scale demonstration of the Am/Cm pretreatment process was performed using a simulated solution with an elemental concentration representative of Tank 17.1. The composition of the simulant was based on the analysis of samples from the tank in 1993 and 1998. The most recent analyses were used to prepare the simulant for elements analyzed at both times. A summary of the element masses and concentrations, based on a solution volume of 15,000 L, is presented in Table 1.

Table 1 Composition of Tank 17.1

Element	Mass (g)	Concentration ^(a) (g/L)
Americium	9,154	0.610
Curium	2,381	0.159
Plutonium	8,916	0.594
Uranium	2,205	0.147
Lanthanum	14,770	0.985
Cerium	11,610	0.774
Praseodymium	9,918	0.661
Neodymium	28,490	1.899
Samarium	6,753	0.450
Europium	1,372	0.091
Gadolinium	3,482	0.232
Aluminum	16,410	1.094
Calcium	999	0.067
Chromium	5,909	0.394
Iron	72,800	4.853
Potassium	3,255	0.217
Manganese	3,641	0.243
Sodium	8,242	0.549
Nickel	4,326	0.147
Total	214,633	14.307

(a) Solution concentrations based on a 15,000 L volume

Elements with a total mass less than approximately 1000 g were not included in the simulant. During preparation of the simulant, equal molar concentrations of the corresponding lanthanides (europium and gadolinium) were used as surrogates for the Am/Cm. The presence of chromium in Tank 17.1 was not simulated to prevent the addition of hazardous material to the surrogate solution. An equal molar concentrations of iron was added to simulated the solution chemistry of

chromium during the pretreatment process. The use of europium and gadolinium as surrogates for Am/Cm and the substitution of iron for chromium is consistent with the preparation of surrogate solutions used during the Am/Cm pretreatment development program.[4]

The surrogate solution was prepared by initially dissolving the target amounts of the nonradioactive nitrate salts in 1M nitric acid, transferring the solution to a 1 L volumetric flask, and filling the flask with 1M nitric acid. A summary of the starting materials used to prepare the solution, the target and actual masses of reagents, and the final concentrations is provided in Appendix A. The surrogate solution used in the solubility experiment was then prepared by adding the target amount of uranyl nitrate hexahydrate (UNH) and a measured aliquot of a nitrate solution containing 34 g/L plutonium to 500 mL of the nonradioactive solution. The concentrations of uranium and plutonium in the surrogate are summarized in Appendix A.

The pretreatment solubility experiment was performed using a 1 L, three-neck flask shown schematically on Figure 3. The bottom of the flask was slightly flattened to facilitate heating on a hot plate. Agitation was provided by a magnetic stirring bar. A graduated addition funnel with stopcock was used to add acid solutions at a controlled rate during the pretreatment process. The temperature of the precipitation vessel was monitored by inserting a calibrated thermometer into the flask. The oxalate precipitation was performed by adding a 250 mL aliquot of the simulated Tank 17.1 solution to the flask, heating the solution to 60°C, and adding 150 mL of 0.9M oxalic acid over approximately 15 min. The excess oxalic acid concentration was 0.3M based on the prepared concentrations and complete precipitation of the lanthanide elements and plutonium. During the oxalic acid addition, the solution was stirred using the magnetic stirring bar. Once the oxalic acid addition was complete, the flask contents were cooled to 45°C (with continual stirring) and digested for 4 hr. Following the digestion period, the flask contents were cooled to 35°C and allowed to settle for 1 hr. The solution was held at 35°C to simulate radiolytic heating during the pretreatment of the actual material. Three 9.4 mL samples of the precipitation supernate were removed from the flask using a 10 mL disposable syringe. The solution was expelled through an 0.45 µm filter disk into a small plastic sample bottle.

Following removal of the samples, a volume of supernate approximately equal to the precipitant volume (minus the sample volume) was removed from the flask. The solution was transferred using a dip leg inserted into the flask which was connected to a receipt bottle under vacuum (see Figure 3). The depth of the dip leg was calibrated to leave approximately 250 mL of solution in the flask. After cooling overnight to 19°C, a fine precipitate was seen in the sample bottles and the receipt bottle. The precipitate in the sample bottles was dissolved by pipetting a 2 mL aliquot of concentrated (15.7M) nitric acid into each bottle. Concentration errors associated with changes in the density of the sample as a function of temperature were ignored due to the much larger uncertainties associated with the trace metal and radiochemical analyses. Three additional samples of the precipitation supernate were removed from the receipt bottle at 19°C using the same sampling procedure to allow a comparison with the solubility data at 35°C.

In preparation for the first washing step, the precipitate and remaining supernate were stirred and heated to 35°C. The precipitate was then washed using a 250 mL aliquot of 0.25M oxalic acid/0.5M nitric acid solution. The wash solution was added using the addition funnel over approximately 15 min. Once the addition was complete, the solution was stirred for an additional 15 min and allowed to settle for 1 hr. Three 9.4 mL samples of the wash solution supernate were removed from the flask using the sampling procedure discussed above. After sampling, supernate was transferred from the flask using the dip leg leaving an approximate 250 mL volume in the flask. After cooling overnight to 18.5°C, a fine precipitate was seen in the sample bottles and supernate removed from the precipitation vessel. The precipitate in the sample bottles was dissolved by pipetting a 2 mL aliquot of 15.7M nitric acid into each bottle. A second set of samples was removed from the transferred supernate (at 18.5°C) to allow a comparison with the solubility data at 35°C.

The precipitate wash procedure was repeated a second time following the same steps discussed above. Three 9.4 mL samples of supernate were removed prior to transferring solution from the flask. After cooling overnight to 16.5°C, precipitates were present in both the sample bottles and transferred supernate. The precipitate in the sample bottles was dissolved by pipetting a 2 mL aliquot of concentrated nitric acid into each bottle. Three additional samples of the transferred supernate were removed at 16.5°C to allow a comparison with the solubility data at 35°C. The precipitate slurry remaining in the flask was dissolved in nominally 8M nitric acid by adding a 250 mL aliquot of 15.7M nitric acid over approximately 45 min and heating at 65°C for 30 min. After cooling overnight to 18°C, three 9.4 mL samples of the solution were removed for analysis. No solids were present in the flask. The final volume of solution following sample removal was 452 mL. A summary of the solution volumes added and removed from the precipitation flask during the pretreatment process is provided in Appendix B.

Results and Discussion

The analytical results for the pretreatment solubility experiment are summarized in Table 2. The concentrations given in the table are the average results from the analysis of triplicate samples taken at each sampling point during the pretreatment experiment. Plutonium analyses were performed by liquid scintillation counting using a gamma scan to correct the total alpha activity for americium-241. The lanthanide elements, aluminum, calcium, iron, manganese, sodium, and nickel were determined by induction-coupled plasma emission spectroscopy (ICP-ES). Potassium was determined by atomic absorption spectroscopy (AAS) and uranium by pulsed laser fluorometry. The data reported in Table 2 reflect the necessary dilutions made to dissolve the solids precipitated during sample cooling.

The concentrations for the Tank 17.1 simulant listed in Table 2 include values for each element calculated from the mass of the starting materials (see Appendix A) and the experimentally measured values. The difference between the two concentrations was generally less than 10%. The largest differences were associated with the hydrated nitrate salts (i.e. lanthanide elements and iron) and were likely biased low due to the absorption of moisture by the salts. The measured concentrations were used in all subsequent calculations presented in Table 2.

The solubility of the plutonium (IV) oxalate in the precipitation supernate was 10 $\mu\text{g/mL}$ at 35°C. The corresponding solubility in 0.63M nitric acid with 0.3M excess oxalic acid can be estimated from Figure 2 as approximately 110 $\mu\text{g/mL}$ at 26.5°C. In addition to the temperature effect, the large decrease in solubility can be attributed to coprecipitation with the lanthanide elements. The ionic radii of the lanthanide elements and plutonium are quite similar.[5] Random substitution of these elements in the oxalate crystal lattice will occur reducing the solubility normally seen for plutonium (IV) oxalate in pure nitric acid solution. Plutonium (IV) coprecipitates quite completely with lanthanum oxalate from approximately 0.1M nitric acid/0.1M oxalic acid, but further increase in the oxalate concentration yields less effective coprecipitation due to the formation of soluble plutonium (IV) oxalate complexes.[2]

The solubility of the lanthanide elements given in Table 2 reflect the same general trend observed during the Am/Cm pretreatment development program;[4] although, the measured solubilities for the elements were somewhat higher. To illustrate this trend, solubility data for selected lanthanide elements from the pretreatment development program are plotted on Figure 4. From this figure, one can see that the solubility of the lanthanide elements tend to decrease with increasing atomic number. The exception to this rule is neodymium which became more soluble

Table 2 Oxalate Solubility Data for Am/Cm Pretreatment

Insoluble Oxalates								
	La ($\mu\text{g/mL}$)	Ce ($\mu\text{g/mL}$)	Pr ($\mu\text{g/mL}$)	Nd ($\mu\text{g/mL}$)	Sm ($\mu\text{g/mL}$)	Eu ($\mu\text{g/mL}$)	Gd ($\mu\text{g/mL}$)	Pu ($\mu\text{g/mL}$)
<u>Simulant</u>								
Makeup	983	773	661	1900	451	463	326	200
Analysis	927	763	641	1783	417	423	308	221
<u>Supernate</u>								
Analysis (35°C)	145	51	23	45	9.3	7.3	6.3	10
Analysis (19°C)	98	26	8.5	14	3.4	1.4	1.8	0.5
<u>1st Wash</u>								
Analysis (35°C)	43	11	3.3	7.3	1.8	1.0	1.0	2.7
Analysis (18.5°C)	40	9.2	3.0	5.0	1.8	0.6	0.9	1.8
<u>2nd Wash</u>								
Analysis (35°C)	16	5.5	<1.5	4.4	1.0	0.7	0.6	4.0
Analysis (16.5°C)	14	3.6	0.5	2.7	0.8	0.4	0.5	3.5
<u>Feed</u>								
Analysis	410	373	318	893	209	216	158	106
Calculated ^(a)	483	397	334	928	217	220	160	115

(a) Calculated values assume 100% recovery.

Table 2 Continued

Soluble Oxalates

	U ($\mu\text{g/mL}$)	Al ($\mu\text{g/mL}$)	Ca ($\mu\text{g/mL}$)	Fe ($\mu\text{g/mL}$)	K ($\mu\text{g/mL}$)	Mn ($\mu\text{g/mL}$)	Na ($\mu\text{g/mL}$)	Ni ($\mu\text{g/mL}$)
<u>Simulant</u>								
Makeup	612	1094	67	5277	219	243	552	288
Analysis	613	1041	64	5669	212	217	532	258
<u>Supernate</u>								
Analysis (35°C)	388	620	39	3289	139	137	324	169
Analysis (19°C)	370	648	40	3686	133	139	338	173
Calculated ^(b)	383	650	40	3543	132	136	333	162
<u>1st Wash</u>								
Analysis (35°C)	198	312	20	1698	68	70	164	87
Analysis (18.5°C)	183	332	22	1665	67	74	173	91
Calculated ^(b)	193	327	20	1781	67	68	167	81
<u>2nd Wash</u>								
Analysis (35°C)	97	155	10	844	33	35	82	43
Analysis (16.5°C)	91	161	11	828	32	36	84	44
Calculated ^(b)	95	162	10	882	33	34	83	40
<u>Feed</u>								
Analysis	54	99	7.9	423	17	18	44	23
Calculated ^(b)	52	89	5.5	484	18	19	45	22

(b) Calculated values assume complete solubility.

than cerium and praseodymium at lower oxalic acid concentrations. Similar behavior for neodymium was also seen in the pretreatment solubility experiment. The measured solubility for neodymium was higher than the solubility of praseodymium and approximately equal to the solubility of cerium. The increase in the solubilities of the lanthanide elements (compared to values measured during the Am/Cm pretreatment development program) could be explained by the way the precipitation flask was heated during the solubility experiment. Using a hot plate to heat the flask from the bottom would create a temperature gradient in the flask, especially when the stirrer was off during the time the relatively small volume of precipitate was allowed to settle. The higher temperature near the bottom of the flask may have increased the solubility of these elements. The precipitation flask during the Am/Cm pretreatment development program was totally immersed in a water batch which would maintain a more uniform temperature in the precipitate slurry.

The effect of temperature on the oxalate solubility of the lanthanide elements and plutonium during pretreatment can be seen in Table 2. A 16°C decrease in temperature had a significant impact on the solubilities in the precipitation supernate, reducing the lanthanide solubilities by a factor of 1.5 to 5.2 and plutonium solubility by a factor of 20. The effect of temperature on the oxalate solubilities was not as pronounced in the two wash solutions. This can be attributed to a decrease in the nitric acid concentration during the two washes which reduced the solubilities. The measured concentrations were also nearing or at the detection limits of the ICP-ES.

As expected, uranium and the alkali, alkaline earth, and transition metal impurities in the Tank 17.1 simulant were soluble throughout the pretreatment process. The measured concentrations in the precipitation supernate and the wash solutions can be accurately predicted by taking into account the dilution effects and the removal of the supernate and wash solutions from the precipitation flask. The calculated concentrations in Table 2 were estimated using this procedure. A decrease in temperature had no effect on the concentrations measured in the precipitation supernate or the wash solutions for these elements.

Using the concentrations given in Table 2 and the volumes of solution added and removed from the precipitation flask during the pretreatment experiment (reported in Appendix B), material balances were performed for each element in the Tank 17.1 simulant. For each element, the percentage of the mass recovered following dissolution of the oxalate precipitate and the percentages lost to the precipitation supernate and wash solutions are given in Table 3. The material balance closure for each element, calculated as the percentage of the element in Tank 17.1 simulant, is also presented.

The material balances for the lanthanide elements and plutonium reiterate that solubility losses for these elements will be reasonably low during the pretreatment process. Losses of Am/Cm should differ little from the losses of the europium and gadolinium surrogates used in the simulated solution. Coprecipitation of plutonium (IV) with the lanthanide and Am/Cm oxalates will also minimize solubility losses of plutonium with greater than 94% of the element reporting to the vitrification feed solution. The plutonium recovery does not take into account transfer losses such as entrainment of oxalate solids during precipitate washes; however, the ratio of the plutonium recovery to the recovery of the lanthanides (and Am/Cm) should change very little. Preferential separation of plutonium from other insoluble oxalates will not occur during solution transfer operations.

The recovery of uranium and the alkali, alkaline earth, and transition metal impurities ranged from approximately 15 to 22%. Based on the dilution effects and the volumes of supernate and wash solutions removed during the experiment, the theoretical recovery was 16%. Of the 84% of the soluble oxalates theoretically removed during the pretreatment experiment, 37% was removed in the precipitation supernate, 32% was removed in the first wash solution, and 14% was removed in the second wash solution. The removal of metal impurities from the actual Am/Cm solution during pretreatment operations should be close to these values assuming the additions of precipitant and wash solution and removals of supernate are proportional to the volumes used during the pretreatment experiment.

Table 3 Material Balances for Am/Cm Pretreatment

Insoluble Oxalates

	La (%)	Ce (%)	Pr (%)	Nd (%)	Sm (%)	Eu (%)	Gd (%)	Pu (%)
Element Recovered	84.5	93.8	97.3	97.8	98.0	98.6	98.3	94.3
Element Lost	15.5	6.2	2.7	2.2	2.0	1.4	1.7	5.7
Precipitation Supernate	9.2	4.0	2.2	1.5	1.3	1.0	1.2	2.7
1 st Wash Solution	4.8	1.5	0.5	0.4	0.5	0.2	0.3	1.3
2 nd Wash Solution	1.6	0.7	0.0	0.2	0.2	0.2	0.2	1.7
Material Balance Closure	100.5	100.1	97.9	98.3	98.3	99.6	99.9	98.0

Soluble Oxalates

	U (%)	Al (%)	Ca (%)	Fe (%)	K (%)	Mn (%)	Na (%)	Ni (%)
Element Recovered	16.6	18.7	22.0	15.4	15.3	15.9	16.3	16.2
Element Lost	83.4	81.3	78.0	84.6	84.7	84.1	83.7	83.8
Precipitation Supernate	36.5	35.8	33.7	36.7	38.2	36.7	36.7	36.4
1 st Wash Solution	32.6	31.4	30.2	33.1	32.3	32.7	32.4	32.6
2 nd Wash Solution	14.3	14.0	14.0	14.8	14.2	14.7	14.5	14.7
Material Balance Closure	102.1	98.1	107.0	93.1	101.7	101.5	97.8	105.6

Since the beta decay of plutonium-241 provides a constant in-growth of americium in weapons grade plutonium, the fate of americium during the Am/Cm pretreatment process can be followed using a trace level material balance. The mass of americium-241 was calculated using the gamma scans for the samples taken during the pretreatment experiment. Table 4 provides a summary of the americium mass in the simulated Tank 17.1 solution and the amounts recovered and lost during the pretreatment operations. An americium material balance, presented in the table, gives the percentage of the mass recovered following dissolution of the oxalate precipitate and the percentages lost to the precipitation supernate and wash solutions. The material balance closure was 99.3% calculated as the percentage of the americium in the simulated solution. The recovery of greater than 97% of the americium in the dissolved oxalate precipitate is consistent with the recovery of europium, the surrogate for americium in the simulated solution.

Table 4 Pretreatment Material Balance for Americium

	Mass (mg)	Total (%)
Americium in Simulant	1.24×10^{-6}	
Americium Recovered	1.20×10^{-6}	97.5
Americium Lost	3.12×10^{-8}	2.5
Precipitation Supernate	1.72×10^{-8}	1.4
1 st Wash Solution	9.53×10^{-9}	0.8
2 nd Wash Solution	4.46×10^{-9}	0.4
Material Balance Closure		99.3

Melter Feed Preparation

Experimental

The preparation of an oxalate slurry feed for the batch vitrification flowsheet was simulated by preparing a surrogate solution based on the elemental concentrations predicted by a pretreatment material balance. A summary of the element masses and concentrations, based on a solution volume of 1,166 L, is presented in Table 5.

Table 5 Composition of Pretreated Am/Cm Solution

Element	Mass (g)	Concentration ^(a) (g/L)
Americium	8869	7.61
Curium	2182	1.87
Plutonium	2238	1.92
Uranium	165	0.14
Lanthanum	14668	12.58
Cerium	11557	9.91
Praseodymium	9900	8.49
Neodymium	28463	24.41
Samarium	6727	5.77
Europium	6918	5.93
Gadolinium	4885	4.19
Aluminum	297	0.25
Calcium	18	0.02
Chromium	107	0.09
Iron	1315	1.13
Potassium	59	0.05
Manganese	7175	6.15
Sodium	149	0.13
Nickel	78	0.07
Total	98816	84.75

(a) Solution concentrations based on a 1,166 L volume

The surrogate solution was prepared in the same manner as the simulated Tank 17.1 solution. Equal molar concentrations of europium, gadolinium, and iron were used as the surrogates for Am/Cm and chromium, respectively. The solution was prepared by initially dissolving the target amounts of nonradioactive nitrate salts in 1M nitric acid, transferring the solution to a 1 L volumetric flask, and filling the flask with 1M nitric acid. A summary of the starting materials used to prepare the solution, the target and actual masses of reagents, and the final concentrations is provided in Appendix A. The additions of plutonium and uranium were made to a 500 mL

volume of the nonradioactive solution. Uranium was added as UNH and plutonium as a measured aliquot of a nitrate solution containing 85 g/L plutonium. The concentration of plutonium in the simulated solution was based on the results from the pretreatment solubility experiment. The concentrations of uranium and plutonium in the surrogate are given in Appendix A.

A simulation of the feed preparation step for the batch vitrification flowsheet was performed using the same laboratory equipment as the pretreatment solubility experiment (see Figure 3). Initially, a 250 mL aliquot of the pretreated Am/Cm simulant was added to the precipitation flask. The solution was heated to 60°C and stirred using the hot plate and magnetic stirring bar. An oxalate precipitation was performed by adding 445 mL of 0.9M oxalic acid over approximately 20 min. The excess oxalic acid concentration was 0.3M based on the prepared concentrations and complete precipitation of the lanthanide elements and plutonium. Once the oxalic acid addition was complete, the flask contents were cooled to 45°C (with continual stirring) and digested for 4 hr. Following the digestion, the flask contents were cooled to 35°C to simulate radiolytic heating and allowed to settle for 1 hr. Three 9.2 mL samples of the precipitation supernate were removed from the flask using a 10 mL disposable syringe. The solution was expelled through an 0.45 μ m filter disk into a small plastic sample bottle. To prevent precipitation of the lanthanide elements and plutonium, 2 mL of 15.7M nitric acid were transferred by pipette to the sample bottles before adding the precipitation supernate. Following sample removal a volume of supernate equal to the precipitant volume (minus the sample volume) was removed from the flask using the solution transfer system. After cooling overnight to 19°C, a fine precipitate was present in the plastic storage bottle. Three additional samples of supernate were removed from the bottle to allow a comparison of solubility data at 35°C.

To prepare for a single oxalic acid wash, the precipitate slurry was stirred and heated to 35°C. A 250 mL aliquot of 0.1M oxalic acid was added to the flask using the addition funnel over approximately 20 min. Once the addition was complete, the solution was stirred for an additional 15 min and allowed to settle for 1 hr. Three 9.2 mL samples of the wash solution supernate were removed from the flask using the sampling procedure discussed above. To prevent precipitation, 2 mL of 15.7M nitric acid were transferred by pipette to the bottles before adding the sample. After sampling, supernate was transferred from the flask using the solution transfer system leaving approximately 250 mL in the flask. After cooling overnight to 23°C, a second set of 3 samples was removed from the transferred supernate which contained a fine precipitate on the bottom of the storage bottle.

In order to perform material balances for the lanthanide elements and plutonium, the oxalate precipitate generated during the simulated vitrification feed preparation was dissolved. The dissolution procedure for the precipitate was the same as employed for the precipitate generated during the pretreatment experiment. The dissolution process was initiated by adjusting the nitric acid concentration to nominally 8M by slowly adding a 250 mL aliquot of 15.7M nitric acid over approximately 1 hr, stirring, and heating at 65°C. An air-cooled condenser was attached to the flask to reduce evaporation losses during heating. A 16 hr oxalate digestion was performed before three 9.2 mL samples were removed from the precipitation flask. Following the extended

digestion period, the solution appeared clear except for a small amount of solids which were assumed to be silica from the degradation of the glass precipitation vessel. However, the closure of a preliminary plutonium material balance was poor (65%). Inspection of the storage bottle containing the digested solution revealed the presence of a red precipitate on the bottom. The solution and solids were transferred back to the precipitation flask to continue the oxalate digestion. A 1 mL aliquot of concentrated (28.9M) hydrofluoric acid was added to the flask to aid in the dissolution. The resulting fluoride concentration was nominally 0.065M based on the measured volume of solution. The flask was stirred and heated to 65°C for approximately 24 hr over a 4 day period. During this time all solids dissolved. Three 9.4 mL samples were removed from the flask for analysis. The final volume of solution following sample removal was 407 mL. A summary of the solution volumes added and removed from the precipitation flask during the feed preparation and dissolution processes is provided in Appendix B.

Results and Discussion

The analytical results for the melter feed preparation experiment are summarized in Table 6. The concentrations given in the table are the average results from the analysis of triplicate samples. The elemental analyses were performed using the same methods as described for the pretreatment experiment; however, interference problems were encountered with the ICP-ES analysis due to the high lanthanide concentrations. The data reported in Table 6 reflect the necessary dilutions made to prevent the precipitation of samples upon cooling.

Table 6 Oxalate Solubility Data for Melter Feed Preparation

Insoluble Oxalates								
	La (µg/mL)	Ce (µg/mL)	Pr (µg/mL)	Nd (µg/mL)	Sm (µg/mL)	Eu (µg/mL)	Gd (µg/mL)	Pu (µg/mL)
<u>Simulant</u>								
Makeup	12580	9912	8491	24411	5770	5933	4189	2040
Analysis	12640	10508	8978	24382	6333	5790	4188	2138
<u>Supernate</u>								
Analysis (35°C)	69	9.5	5.9	9.3	<2.3	1.6	1.8	21
Analysis (22.5°C)	64	6.6	3.7	6.7	<2.3	1.2	1.1	18
<u>Oxalic Acid Wash</u>								
Analysis (35°C)	9.4	4.1	3.5	3.9	<2.3	0.6	0.7	21
Analysis (23°C)	8.2	<3.20	<1.5	<1.6	<2.3	0.3	<0.4	21
<u>Melter Feed</u>								
Analysis	6584	5458	4614	12962	3273	3031	2208	1099
Calculated ^(a)	6744	5606	4790	13008	3379	3089	2234	1141

(a) Calculated values assume 100% recovery.

Table 6 Continued

Soluble Oxalates

	U ($\mu\text{g/mL}$)	Al ($\mu\text{g/mL}$)	Ca ($\mu\text{g/mL}$)	Fe ($\mu\text{g/mL}$)	K ($\mu\text{g/mL}$)	Mn ($\mu\text{g/mL}$)	Na ($\mu\text{g/mL}$)	Ni ($\mu\text{g/mL}$)
<u>Simulant</u>								
Makeup	142	254	15	1226	50	6153	128	67
Analysis	160	752 ^(b)	48 ^(b)	1253	47	6286	175	97
<u>Supernate</u>								
Analysis (35°C)	52	90	7.6	442	17	2255	47	30
Analysis (22.5°C)	49	89	7.6	441	17	2285	47	29
Calculated ^(c)	58	91 ^(d)	5.6 ^(d)	451	17	2261	63	35
<u>Oxalic Acid Wash</u>								
Analysis (35°C)	25	42	3.8	215	8.8	1104	23	15
Analysis (23°C)	24	44	3.9	222	8.2	1103	23	14
Calculated ^(c)	28	45 ^(d)	2.7 ^(d)	222	8.3	1115	31	17
<u>Feed</u>								
Analysis	21	286 ^(b)	18 ^(b)	113	4.2	518	29	15
Calculated ^(c)	15	24 ^(d)	1.5 ^(d)	119	4.4	598	17	9.2

(b) Measured value biased high due to interferences with lanthanide elements.

(c) Calculated values assume complete solubility.

(d) Calculated using the element makeup concentration.

The concentration of each element in the pretreated Am/Cm surrogate, calculated from the mass of the starting material (see Appendix A), is also presented in Table 6. The difference between the "makeup" and experimentally measured concentrations for the lanthanides and plutonium are in good agreement with the difference in the concentrations being less than 9% for all elements; although, the measured lanthanide concentrations do appear biased higher than the "makeup" concentrations. This observation is in contrast to the measured lanthanide concentrations in the simulant prepared for the pretreatment experiment which appeared biased lower than the "makeup" concentrations presumably due to the absorption of moisture by the nitrate salts. The high bias in the lanthanide concentrations for the pretreated Am/Cm surrogate suggests that spectral interferences between these elements likely exists at high concentrations.

Spectral interferences also influenced the concentrations for several metal impurities. The concentrations of aluminum and calcium, and to a lesser extend sodium and nickel were high when compared to the "makeup" concentrations. To verify that interferences from the lanthanide elements contributed to the positive bias in these concentrations, a 10 mL sample of the pretreated Am/Cm surrogate was precipitated with 25 mL of oxalic acid to remove the majority of the lanthanide elements from solution. Duplicate samples of the supernate were then analyzed

by ICP-ES for the metal impurities (excluding uranium and potassium). Two samples of the untreated surrogate were also analyzed for sodium by AAS. The results from these analyses are compared with the "makeup" concentrations and the original analysis in Table 7.

Table 7 Analysis of Am/Cm Surrogate Following Oxalate Precipitation

	Al ($\mu\text{g/mL}$)	Ca ($\mu\text{g/mL}$)	Fe ($\mu\text{g/mL}$)	Mn ($\mu\text{g/mL}$)	Na ($\mu\text{g/mL}$)	Na ($\mu\text{g/mL}$)	Ni ($\mu\text{g/mL}$)
Makeup	254	15	1226	6153	128	128	67
1 st Analysis	752	48	1253	6286	175 ⁽¹⁾	N/A	97
2 nd Analysis	301	14	1288	5863	218 ⁽¹⁾	199 ⁽²⁾	71

(1) Analyzed by ICP-ES.

(2) Analyzed by AAS.

The elemental analysis of the treated sample clearly showed a reduction in the concentrations of aluminum, calcium, and nickel. Therefore, the positive bias in the original analyses can be at least partially attributed to spectral interferences due to the high lanthanide concentrations. The results from the sodium analyses were inconclusive. Neither analytical method showed the expected decrease in the sodium concentration suggesting there could be other problems with the analysis. The measured concentrations shown in Table 6 for all of the elements except aluminum and calcium were used for subsequent calculations presented in the table. For aluminum and calcium, the "makeup" concentrations were used for these calculations.

The solubility of the plutonium (IV) oxalate in the precipitation supernate was 21 $\mu\text{g/mL}$ at 35°C. This value is approximately a factor of 2 higher than the concentration measured in the precipitation supernate during the pretreatment solubility experiment. The difference in the measured concentration can be attributed to differences in the ionic strength of the solutions. The nitrate concentration in the pretreated Am/Cm surrogate was much higher than the concentration in the Tank 17.1 simulant due to the high lanthanide concentrations. The higher nitrate concentration should increase the plutonium solubility due to increased complexation.

The relative solubilities for the lanthanide elements shown in Table 6 are consistent with the solubility measurements made during the pretreatment experiment and the Am/Cm pretreatment development program (see Figure 4); although, the actual values are less. The decrease in solubilities of the lanthanide oxalates compared to the solubilities measured during these experiments can be attributed to a decrease in the nitric acid concentration due to the dilution by the larger volume of oxalic acid required for precipitation. The effect of temperature on the solubility of the lanthanides and plutonium was not as pronounced as seen during the pretreatment experiment presumably due to the lower nitric acid concentration.

Simulation of the melter feed preparation process provided an additional demonstration that uranium and the alkali, alkaline earth, and transition metal impurities in the Tank 17.1 solution are soluble in oxalic acid under these conditions. Table 6 provides a comparison of the measured and calculated concentrations for these elements at each step in the process assuming complete solubility. The measured and calculated values are in good agreement except for the elements where difficulties were encountered with the elemental analyses. As before, a decrease in temperature had no effect on the concentrations measured in the precipitation supernate or oxalic acid wash solution.

Using the concentrations given in Table 6 and the volumes of solution added and removed from the precipitation flask during the melter feed preparation experiment (reported in Appendix B), material balances were performed for each element in the pretreated Am/Cm simulant. For each element, the percentage of the mass recovered following dissolution of the oxalate precipitate and the percentages lost to the precipitation supernate and wash solutions are given in Table 8. The material balance closure for each element, calculated as the percentage of the element in the pretreated Am/Cm simulant, is also given in the table. For the plutonium material balance, it was necessary to use the concentrations measured in the dissolved precipitate following the second digestion to obtain good material balance closure. For the other elements in the simulant, the closure did not improve when the analyses from the second set of dissolved precipitate samples were used to perform the material balance, indicating the red solids observed in the storage bottle were most likely a plutonium oxalate. A plutonium (IV) oxalate dihydrate has been precipitated by the addition of 10% oxalic acid to a solution of plutonium in 7M nitric acid at elevated temperature (50 or 75°C).[6]

The material balances for the lanthanide elements and plutonium showed minimal solubility losses during the oxalate precipitation and wash steps used to simulate the preparation of feed for a batch melter. Greater than 99% of the europium and gadolinium, the surrogates for Am/Cm, were recovered during the solubility experiment. The recovery of plutonium during the simulated feed preparation was greater than 97% leading to an estimate that nominally 92% of the plutonium in Tank 17.1 will report to the glass. This estimate takes into account the solubility losses during the pretreatment and melter feed preparation, but, does not include any estimate of material loss during the transfer of solution during these processes.

The closure of the material balances for several of the alkali, alkaline earth, and transition metal impurities (see Table 8) were much poorer than the closure of material balances for the simulated pretreatment process. The poor closure was attributed to problems encountered during the analysis of these elements in the pretreated Am/Cm surrogate and the dissolved oxalate precipitate. The recovery of the soluble oxalates ranged from approximately 14 to 29%. Based on the dilution effects and the volumes of supernate and wash solution removed during the experiment, the theoretical recovery was nominally 18%. Of the 82% of the soluble oxalates theoretically removed during the melter feed preparation, 65% were removed in the precipitation supernate, and 17% were removed in the oxalic acid wash solution.

Table 8 Material Balances for Melter Feed Preparation

Insoluble Oxalates

	La (%)	Ce (%)	Pr (%)	Nd (%)	Sm (%)	Eu (%)	Gd (%)	Pu (%)
Element Recovered	98.9	99.8	99.8	99.9	100.0	99.9	99.9	97.3
Element Lost	1.1	0.2	0.2	0.1	0.0	0.1	0.1	2.7
Precipitation Supernate	1.0	0.2	0.1	0.1	0.0	0.1	0.1	1.8
Oxalic Acid Wash	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.9
Material Balance Closure	98.7	97.5	96.5	99.7	96.9	98.2	98.9	97.8

Soluble Oxalates

	U (%)	Al (%)	Ca (%)	Fe (%)	K (%)	Mn (%)	Na (%)	Ni (%)
Element Recovered	24.7	18.3	13.7	17.4	16.4	15.9	33.9	28.7
Element Lost	75.3	81.7	86.3	82.6	83.6	84.1	66.1	71.3
Precipitation Supernate	59.9	65.4	67.9	65.5	65.8	66.6	52.4	56.5
Oxalic Acid Wash	15.3	16.4	18.5	17.1	17.7	17.5	13.7	14.8
Material Balance Closure	97.8	97.5	130.4	97.3	102.5	97.3	92.4	98.0

An americium material balance was also performed for the melter feed preparation experiment using the americium-241 produced from the beta decay of plutonium-241. Table 9 provides a summary of the americium mass in the pretreated Am/Cm surrogate, the amounts recovered and lost during the melter feed preparation, and the results from the material balance. The amount of americium recovered in the dissolved precipitate is in excellent agreement with the recovery of europium (the americium surrogate) demonstrated by the material balances in Tables 8 and 9. The overall recovery of americium, predicted by the trace level material balances, for the Am/Cm pretreatment and melter feed preparation processes was greater than 97%. As with plutonium, this estimate takes into account the solubility losses, but, does not include any estimate of material loss during the transfer of solution during these processes.

Table 9 Americium Material Balance for Melter Feed Preparation

	Mass (mg)	Total (%)
Americium in Simulant	1.81×10^{-4}	
Americium Recovered	1.81×10^{-4}	99.9
Americium Lost	2.70×10^{-7}	0.1
Precipitation Supernate	2.05×10^{-7}	0.1
Oxalic Acid	6.46×10^{-8}	0.0
Material Balance Closure		100.0

Conclusions

The pretreatment process planned for preparing the Tank 17.1 Am/Cm solution for vitrification was simulated to measure the solubility of plutonium (IV) oxalate during the processing steps. An oxalate precipitation was initially performed using a simulated solution with europium and gadolinium present as surrogates for the Am/Cm. The plutonium (IV) oxalate solubility in the precipitation supernate was 10 $\mu\text{g/mL}$ (at 35°C). In subsequent precipitate washing steps using 0.25M oxalic acid/0.5M nitric acid, the solubility dropped to less than 5 $\mu\text{g/mL}$. During the precipitation and washing steps, the behavior of the lanthanides, uranium, and alkali, alkaline earth, and transition metal impurities was predictable. The lanthanide oxalates were mostly insoluble with the solubility generally decreasing with increasing atomic number. Uranium and the alkali, alkaline earth, and transition metal impurities were soluble throughout the pretreatment process. The concentration of these elements were accurately predicted using the simulant concentration and volumes of reagents added and supernate removed from the precipitation vessel.

Following the precipitation washing steps, the oxalate precipitate was dissolved allowing elemental material balances to be performed for the pretreatment process. Greater than 94% of the plutonium was recovered in the dissolved precipitate. The recoveries of the lanthanide oxalates were generally 94% or higher except for lanthanum for which the recovery was only 84% due to the higher solubility of its oxalate salt. The recovery of uranium and the alkali, alkaline earth, and transition metal impurities ranged from 15 to 22%. Based on the dilution effects and the volumes of supernate and wash solutions removed during the experiment, the theoretical recovery was 16%. A trace level material balance was also performed for americium using the americium-241 daughter from the decay of plutonium-241. Greater than 97% of the americium was recovered in the dissolved precipitate which is consistent with the recovery of europium, the surrogate for americium in the simulated solution. The material balance closure was very good for all elements.

In a subsequent experiment, the solubility of plutonium (IV) oxalate was measured during a simulation of the flowsheet for preparation of an oxalate slurry feed for vitrification of the pretreated Am/Cm. The measured solubility following an oxalate precipitation of the surrogate solution was 21 $\mu\text{g/mL}$ (at 35°C). The increase in solubility compared to the value measured during the pretreatment experiment (10 $\mu\text{g/mL}$) was attributed to the increased nitrate concentration and ensuing increase in plutonium complexation. The solubility of the plutonium following a precipitant wash with 0.1M oxalic acid was unchanged. The solubility of the lanthanide elements decreased in both the precipitation supernate and wash solution compared to values measured during the pretreatment experiment. The lower solubilities were primarily due to a decrease in the nitric acid concentration as result of the increased volume of oxalic acid required for the precipitation. Uranium and the alkali, alkaline earth, and transition metal impurities were soluble during the simulated feed preparation as expected.

Dissolution of the oxalate precipitate following preparation of the simulated melter feed allowed the performance of elemental material balances. The recovery of plutonium from the precipitate slurry was greater than 97% allowing an estimation that approximately 92% of the plutonium in Tank 17.1 will report to the glass. Greater than 99% of the lanthanide elements in the pretreated surrogate were recovered from the precipitate slurry. Material balances for uranium and the alkali, alkaline earth, and transition metal impurities showed recoveries of these elements ranging from 14 to 29%. The theoretical recovery, based on the solubility, dilution effects, and volumes of supernate and wash solution removed during the experiment, was approximately 18%. The difference between the measured and theoretical values was the result of problems with the elemental analyses, primarily due to spectral interferences from the high lanthanide concentrations. An americium material balance performed using gamma pulse height analyses for americium-241 showed the recovery of greater than 99.9% of the americium from the precipitate slurry. This value was consistent with the recovery of europium, the surrogate for americium, during the simulation. The overall recovery of americium from the pretreatment and feed preparation processes was greater than 97%, a value also consistent with the measured europium recovery.

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Figure 1 Am/Cm Pretreatment in F-Canyon

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Figure 2 Solubility of Plutonium (IV) Oxalate

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Figure 3 Precipitation Equipment

Precipitation Vessel

Solution Transfer Equipment

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Figure 4 Solubility of Lanthanide Oxalates[4]

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Appendix A Preparation of Simulated Solutions

Table A.1 Simulated Tank 17.1 Solution

Element	Nitrate Salt Starting Material	Target Mass Starting Material (g)	Actual Mass Starting Material (g)	Element Concentration (g/L)
Lanthanum (La)	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	3.0695	3.0650	0.983
Cerium (Ce)	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	2.3986	2.3957	0.773
Praseodymium (Pr)	$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	2.0413	2.0418	0.661
Neodymium (Nd)	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	5.7721	5.7734	1.900
Samarium (Sm)	$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	1.3308	1.3339	0.451
Europium (Eu)	$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	1.3051	1.3050	0.463
Gadolinium (Gd)	$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0.9381	0.9343	0.326
Aluminum (Al)	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	15.2103	15.2124	1.094
Calcium (Ca)	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.3924	0.3936	0.067
Iron (Fe)	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	38.1700	38.1768	5.277
Potassium (K)	KNO_3	0.5611	0.5662	0.219
Manganese (Mn)	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.2682	1.269	0.243
Sodium (Na)	NaNO_3	2.0314	2.0397	0.552
Nickel (Ni)	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.4289	1.4289	0.288
Uranium (U)	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.6437 ^(a)	0.6457 ^(a)	0.612
Plutonium (Pu)	$\text{Pu}^{4+}_{(\text{aq})}$	0.0794 ^(b)	0.102 ^(c)	0.204
Total				14.113

(a) Mass of UNH to prepare 500 mL of surrogate solution

(b) Mass of plutonium required to prepare 500 mL of surrogate solution

(c) Mass of plutonium from 3 mL of a 34 g/L solution added to surrogate solution

Table A.2 Simulated Feed Solution for Am/Cm Vitrification

Element	Nitrate Salt Starting Material	Target Mass Starting Material (g)	Actual Mass Starting Material (g)	Element Concentration (g/L)
Lanthanum	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	39.2144	39.2153	12.58
Cerium	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	30.7166	30.7613	9.93
Praseodymium	$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	26.2133	26.2226	8.49
Neodymium	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	74.1853	74.1864	24.41
Samarium	$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	17.0551	17.0549	5.77
Europium	$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	16.7118	16.7113	5.93
Gadolinium	$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	12.0242	12.0259	4.19
Aluminum	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	3.5356	3.5458	0.26
Calcium	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.0912	0.0954	0.02
Iron	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	8.8715	8.8913	1.23
Potassium	KNO_3	0.1304	0.1315	0.05
Manganese	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	32.1496	32.148	6.15
Sodium	NaNO_3	0.4721	0.4743	0.13
Nickel	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.3320	0.3086	0.06
Uranium	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.1496 ^(a)	0.15 ^(a)	0.14
Plutonium	$\text{Pu}^{4+}_{(\text{aq})}$	0.9598 ^(b)	1.02 ^(c)	2.04
Total				81.38

(a) Mass of UNH to prepare 500 mL of surrogate solution

(b) Mass of plutonium required to prepare 500 mL of surrogate solution

(c) Mass of plutonium from 12 mL of an 85 g/L solution added to surrogate solution

Appendix B Reagent Addition and Removal During Solubility Experiments

Table B.1 Solution Volumes for Am/Cm Pretreatment

Oxalate Precipitation		1 st Wash	
Solution	Volume (mL)	Solution	Volume (mL)
Tank 17.1 Simulant	250	Initial Volume	253
Oxalic Acid	150	Wash Solution	250
Samples Removed	56	Samples Removed	56
Solution Transferred	91	Solution Transferred	201
Total Solution Removed	147	Total Solution Removed	257
Volume Remaining	253	Volume Remaining	245

2 nd Wash		Precipitate Dissolution	
Solution	Volume (mL)	Solution	Volume (mL)
Initial Volume	245	Initial Volume	253
Wash Solution	250	Acid Addition	250
Samples Removed	56	Samples Removed	28
Solution Transferred	175		
Total Solution Removed	231	Total Solution Removed	28
Volume Remaining	264	Volume Remaining	486 ^(a)

(a) The measured volume of solution was 452 mL; the missing solution was attributed to evaporation losses.

Table B.2 Solution Volumes for Vitrification Feed Preparation

Oxalate Precipitation		Oxalic Acid Wash	
Solution	Volume (mL)	Solution	Volume (mL)
Pretreated Simulant	250	Initial Volume	243
Oxalic Acid	445	Wash Solution	250
Samples Removed(a)	28	Samples Removed	55
Solution Transferred	424	Solution Transferred	187
Total Solution Removed	452	Total Solution Removed	242
Volume Remaining	243	Volume Remaining	251

1 st Precipitate Dissolution		2 nd Precipitate Dissolution	
Solution	Volume (mL)	Solution	Volume (mL)
Initial Volume	251	Initial Volume	441
Acid Addition	250	Acid Addition	1
Samples Removed	28	Samples Removed	28
Total Solution Removed	28	Total Solution Removed	28
Volume Remaining	474 ^(b)	Volume Remaining	414 ^(c)

(a) Six samples were removed; however, 3 were removed following measurement of the supernate volume.

(b) The measured volume of solution was 441 mL; the missing solution was attributed to evaporation losses.

(c) The measured volume of solution was 407 mL; the missing solution was attributed to evaporation losses.