Pretreatment of Americium/Curium Solutions for Vitrification(U)

by
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March 1996

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Summary

Vitrification will be used to stabilize an americium/curium (Am/Cm) solution presently stored in F-Canyon for eventual transport to the heavy isotope programs at Oak Ridge National Laboratory. Prior to vitrification, an in-tank oxalate precipitation and a series of oxalic/nitric acid washes will be used to separate these elements and lanthanide fission products from the bulk of the uranium and metal impurities present in the solution. Pretreatment development experiments were performed to understand the behavior of the lanthanides and the metal impurities during the oxalate precipitation and properties of the precipitate slurry. The results of these experiments will be used to refine the target glass composition allowing optimization of the primary processing parameters and design of the solution transfer equipment.

A series of oxalate solubility experiments demonstrated that the uranium (VI) present in the Am/Cm solution is soluble under all anticipated in-tank processing conditions. Experiments were performed using an uranium concentration representative of the canyon tank and with the addition of lanthanum to investigate the co-precipitation of a double salt. Non-radioactive experiments illustrated that the solubility of the lanthanides increased with decreasing excess oxalic acid concentration and that metal impurities will remain soluble during in-tank processing. The majority of the lanthanides and plutonium and essentially all of the Am/Cm will be isolated as a precipitate slurry during the oxalate precipitation. Unwanted, soluble materials, such as uranium, iron, aluminum, and sodium can be removed by decanting and washing with an oxalic/nitric acid solution.

The specific volume of the oxalate slurry and settling behavior of a simulated Am/Cm precipitation were determined to define the in-tank settling time and the length of the solution transfer jet. The specific volume, 0.5 liters per mole of lanthanide/actinide simulant, was measured using non-radioactive surrogates and optimal precipitation conditions. When agitation was stopped, most of the precipitate settled in only a few minutes. The supernate was clear of all but the smallest particles after 30 minutes. The experiment also demonstrated that the precipitate will settle on any horizontal surfaces in a canyon tank such as cooling coils and agitator blades potentially leading to high losses when the supernate is removed. However, once settled to the bottom of the tank, the suction from a steam jet should not disturb the precipitate when placed as close as 1-inch from the top of the oxalate slurry.

Introduction

Background

Approximately 15,000 liters of solution containing isotopes of Am/Cm are currently stored in F-Canyon Tank 17.1 at the Savannah River Site (SRS). These isotopes were recovered during plutonium-242 production campaigns in the mid and late 1970's. The continued storage of these solutions was identified as an item of urgent concern in the Defense Nuclear Facility Safety Board's Recommendation 94-1. Currently there are no existing SRS facilities which can be used to stabilize this material for safe interim storage or transport to the heavy isotope programs at Oak Ridge National Laboratory. An analysis of several alternatives has resulted in the recommendation to stabilize the Am/Cm in a high lanthanide glass. The Multi-Purpose Processing Facility 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 other impurities (primarily iron, aluminum, and sodium) before subsequent vitrification.

The contents of Tank 17.1 were sampled and characterized as part of the analysis of disposition options available for the Am/Cm. When Tank 17.1 was sampled it contained 15,140 liters and approximately 4 M nitric acid. A summary of the chemical analyses are presented in Table 1. The results are reported in mass units due to changes in the solution volume from evaporation and chemical additions. Power generation in the tank is approximately 7 kW.

Pretreatment operations for the Am/Cm stabilization include adjusting the nitric acid concentration of the Tank 17.1 solution to <1M, precipitating the actinides and lanthanides as oxalates, washing soluble metallic impurities from the precipitate slurry, solubilizing the precipitate, and adjusting the nitric acid concentration prior to vitrification. The flowsheet for these operations is based on previous development work and plant operating experience. The recovery of Am/Cm from aluminum and sodium nitrate wastes using this flowsheet was developed by the Savannah River Laboratory (SRL) and a full-scale test was performed in F-Canyon to recover Am/Cm from a Mark 41 target waste solution.[1,2] The flowsheet and operating conditions used during the test are shown on Figure 1 and Table 2, respectively.

Objectives

The Am/Cm pretreatment development program focused on the behavior of the lanthanides and the metallic impurities during the oxalate precipitation and properties of the precipitate slurry. Specific experimental needs included demonstration of the oxalate precipitation to measure the solubility of metallic impurities which have an impact on the glass formulation and measuring the settling rate and specific volume of the precipitate slurry to allow design of the solution transfer equipment. The results of the pretreatment experiments will be used to refine the target glass composition for detailed process design allowing optimization of the primary processing parameters of glass liquidus and viscosity. The settling rate and specific volume of the precipitate slurry are required to define the settling time during in-tank processing and the

minimum height at which the solution transfer jet must be located above the slurry to prevent entrainment of solids.

Experimental

Uranium Solubility Experiments

In order to minimize the handling of radioactive samples, uranium oxalate solubility experiments were performed without simulating the exact chemical composition of Tank 17.1. Two experiments were performed using an uranium concentration representative of the tank. The three remaining experiments were performed with an amount of lanthanum equal to the molar concentration of the lanthanides and actinides (excluding uranium) which are in the tank (i.e. elements which precipitate). These experiments were designed to determine if uranium would co-precipitate as a double salt with insoluble species during in-tank processing. The preparation of the simulated solutions and oxalate precipitate used for these experiments is summarized in Appendices A and B, respectively.

The uranium solubility experiments were performed using a 1 liter, three-neck flask shown schematically on Figure 2. The flask was immersed in a constant temperature bath which was used for temperature control. A graduated addition funnel with stopcock was used to add oxalic acid at a controlled rate. The oxalate precipitations were performed by adding a 250 ml aliquot of simulated solution to the flask, heating the solution to 60°C, and adding a measured volume of 0.9M oxalic acid over 15 to 30 minutes. The excess oxalic acid concentration was varied from 0.3 to 0.6M during 5 experiments. The solution was stirred (at 300 rpm) using a glass stirring rod with 2 sets of paddle blades. Once the oxalic acid addition was complete, the flask contents were cooled to 45°C (with continual stirring) and held for 4 hours. Multiple samples of the precipitation supernate were taken after the flask contents were allowed to settle over night. Samples were removed from the flask using a 10 ml disposable syringe. The solution was then expelled through an 0.45 micron filter disk into the sample bottle. During the first four experiments, the flask contents were allowed to cool over night. The temperature of the supernate was typically between 15 and 20°C. The temperature of the supernate in the final experiment was maintained at 35°C using the constant temperature bath to simulate radiolytic heating in Tank 17.1.

Simulated Am/Cm Pretreatment Experiments

Non-radioactive pretreatment experiments were performed using a simulated solution with elemental concentrations representative of Tank 17.1. Equal molar concentrations of the corresponding lanthanides (samarium, europium, and gadolinium) were used as surrogates for plutonium, americium, and curium. The presence of chromium in Tank 17.1 was not simulated to prevent the generation of a hazardous liquid waste. The solubility of chromium during an oxalate precipitation was assumed to mimic the behavior of other transition metals present in the

tank such as iron and manganese. The technical basis for this assumption is given during the discussion of oxalate solubilities. The preparation of the simulated Tank 17.1 solution for these experiments is summarized in Appendix A.

The pretreatment experiments were performed using a three-neck flask identical to the one used for the uranium solubility experiments (see Figure 2). The oxalate precipitations were performed by adding a 250 ml aliquot of simulated solution to the flask, heating the solution to 60°C with a constant temperature bath, and adding a measured volume of 0.9M oxalic acid over 15 to 30 minutes. The excess oxalic acid concentration was varied from 0.15 to 0.6M during 5 experiments. Preparation of the oxalic acid is summarized in Appendix B. The solution was stirred (at 300 rpm) using a glass stirring rod with 2 sets of paddle blades. Once the oxalic acid addition was complete, the flask contents were cooled to 45°C (with continual stirring) and held for 4 hours. The temperature was then adjusted to 35°C (to simulate radiolytic heating) and the flask contents were allowed to settle over night.

Following the removal of samples using the same technique described for the uranium experiments, 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 tank under vacuum (see Figure 2). The depth of the dip leg was calibrated to leave approximately 250 ml of solution in the flask. The precipitate was then washed using a 250 ml aliquot of 0.25M oxalic acid/0.5M nitric acid solution. The preparation of the wash solution is summarized in Appendix C. The wash solution was added using the addition funnel over 15 to 30 minutes. Once the addition was complete, the solution was stirred for an additional 15 minutes and allowed to settle for 1 hour. A volume of supernate approximately equal to the wash volume was then removed by vacuum transfer. Samples of the wash solution were taken at this time. The wash procedure was repeated 4 times for a total of 5 wash cycles. All washes were performed at 35°C. The precipitate slurry was then dissolved in nominally 8M nitric acid by adding a 250 ml aliquot of concentrated (15.7M) nitric acid and heating at 65°C for 30 minutes. Samples of the dissolved slurry were then taken for analysis.

Slurry Properties of Oxalate Precipitate

Initially, three small-scale scouting experiments (ACP-11, ACP-12, and ACP-13) were conducted in a 1000 ml graduated cylinder to develop the methodology to accurately measure the specific volume of the oxalate slurry. The cylinder was placed on a hot plate with a magnetic stirrer, which was used for both heating and stirring. The oxalic acid was added using the addition funnel used for the Tank 17.1 solubility experiments. A calibrated mercury-filled thermometer was used for temperature measurements. The preparation of the simulated solutions and 0.9M oxalate acid used for these experiments is summarized in Appendices A and B, respectively.

The settling rate and specific volume of the oxalate precipitate slurry were measured using a glass precipitator fabricated from 120-mm tubing with a 150-mm jacket (see Figure 3). The vessel was approximately 530-mm tall. Ports in the precipitator head allowed the insertion of a stirrer, glass thermowell, thermometer, and dip leg for solution transfer. A port was also provided for the addition of oxalic acid and the removal of samples. The stirrer assembly was fabricated from a glass rod with two sets of paddle blades. During equipment testing it was necessary to add an approximate 1-inch thick Teflon™ disk with a centering hole to prevent the stirrer from wobbling. The temperature of the solution inside the precipitator was controlled using a Fisher Scientific Programmable Circulator (Model 9110). The circulator was equipped with a remote sensing probe which was inserted into the glass thermowell. However, a calibrated mercury-filled thermometer was the primary indication of the precipitator temperature.

A 7-mm (OD) tube was originally provided for the removal of supernate from the precipitator. However, the flow resistance of the small-diameter tube was too high to achieve linear fluid velocities comparable to the velocities achieved by canyon solution transfer jets. Velocities in excess of the canyon transfer jets were achieved by using a 10-mm (OD) tube inserted through the precipitator thermowell port. A 9 liter bottle was used as the solution receipt vessel. Vacuum was supplied using a GCA Corporation Precision Vacuum Pump (Model PV35). Solution was transferred by evacuating the receipt vessel and opening a control valve to siphon liquid from the precipitator. The procedure was analogous to the method used to remove the wash solution during the Tank 17.1 solubility experiments. The oxalate precipitate was pumped into the precipitator using a Cole-Parmer Instrument Company Masterflex® pump. A calibrated scale on the outside wall of the inner vessel was used to measure the oxalate slurry volume. The preparation of the simulated Tank 17.1 solution and 0.9M oxalic acid precipitate is summarized in Appendices A and B, respectively.

Discussion

Solubility of Uranyl Oxalate

The analytical results from the uranium solubility experiments are summarized in Table 3. During the five experiments, the oxalic acid concentration was varied from 0.3 to 0.6M. The resulting concentrations of uranium, lanthanum, and nitric acid are listed in the table. The concentration of uranium calculated using the simulant concentrations and the volume of oxalic acid added during the precipitation (assuming complete solubility) is also listed in the table. Comparison of the average uranium concentration measured in the supernate from each precipitation and the calculated value using a t-test shows no statistical difference between the means (see Table 4). This clearly shows that uranium (VI) oxalate is soluble under these conditions. This observation is consistent with the literature, as soluble uranyl oxalate complexes involving mixed compounds, such as aquo-oxalates, aquo-carbonates, aquo-sulfato-oxalates, and aquo-fluoro-oxalates have been reported.[3]

Simulated Am/Cm Pretreatment Experiments

The experimental conditions and analytical results from the simulated Am/Cm pretreatment experiments are summarized in Tables 5-10. Table 5 lists the excess oxalic and final nitric acid concentrations and the number of wash cycles completed for each experiment. The excess oxalic acid concentration was calculated assuming complete precipitation of the lanthanides and complete solubility of the metal impurities. The nitric acid concentration was calculated by taking into account the dilution of the 1M concentration in the simulated solution by the oxalic acid addition. Tables 6-10 summarize the elemental concentrations measured in the supernate, wash solutions, and dissolved melter feed. In general, the concentration for each element is the average of four independent samples analyzed by Inductively-Coupled Plasma Emission Spectroscopy (ICP-ES).

Solubility of Lanthanide and Metal Impurities

As expected, the solubility of the lanthanides increase with decreasing excess oxalic acid in the supernate. The solubility of lanthanum, cerium, praseodymium, neodymium, and europium are plotted on Figure 4 as a function of the excess oxalic and nitric acids. Complete curves for samarium and gadolinium were not plotted since the concentrations at high excess oxalic acid were below the ICP-ES detection limits. From the data at low excess oxalic acid, one would expect the solubility curves for samarium and gadolinium to fall just above and below the solubility curve for europium. The extremely low solubility of the lanthanides at high excess oxalic acid concentrations is consistent with the literature where oxalate precipitation from dilute nitric acid solution is reported as a quantitative and fairly specific separation procedure for the lanthanides, which can be determined gravimetrically, with subsequent ignition to the oxides.[4]

The solubility of americium, curium, and plutonium (IV) oxalates under the conditions expected during the pretreatment operations is well documented in the literature.[5] The solubility data for the three actinides are plotted on Figures 5-7. From the data, it can be seen that the solubilities in 0.3M excess oxalic acid (with the nitric acid concentration adjusted to less than 1M) are less than 10 μg/ml for the Am/Cm and approximately 100 μg/ml for plutonium (IV). Therefore, the oxalate precipitation will provide a slight separation of the plutonium from the Am/Cm and minimal Am/Cm losses.

The concentrations of the metal impurities measured in the oxalate precipitation supernate indicate aluminum, calcium, iron, potassium, manganese, sodium, and nickel are almost completely soluble under the experimental conditions investigated. As a comparison, the concentrations of each element were calculated using the measured concentration in the simulated solution and the dilution provided by the oxalic acid addition. The predicted concentrations, listed in Tables 6-10, are in good agreement with the analyzed supernate concentrations. In addition, the stability constants for all non-alkali elements predict the formation of soluble oxalate complexes (see Table 11).[6] A strong complex is not predicted for potassium, presumably due to steric hindrance which prohibits the relatively large metal ion from

fitting into the cavity (or cavities) provided by the oxalate ligand.[4] Literature data for sodium is unavailable. However, the solubilities of sodium oxalate and potassium oxalate monohydrate in water (at 20°C) are given in the literature as 34 and 360 grams/liter, respectively.[7] Both concentrations are well above concentrations in Tank 17.1 (see Table 1) and the solubility in a 1M nitric acid solution should be even greater due to the suppression of the free oxalate concentration by the disassociation of the stronger nitric acid.

The presence of chromium in Tank 17.1 was not simulated due to the generation of hazardous waste solutions. However, the aqueous chemistry of chromium (III) should be similar to other elements in the first transition series with the same oxiadation state such as iron and manganese (III). From a comparison of the stability constants for iron and manganese (III) (given as approximately 10^{18} in Table 11 for the trioxalato complexes), one would expect a stability constant of similar magnitude for chromium (III). In addition, qualitative information in the literature indicates chromium (III) oxalate is soluble in water,[7,8] and should be even more soluble in dilute nitric acid. This provides strong evidence that chromium will remain soluble during the in-tank processing.

If the concentrations of aluminum and transition metal impurities are increased by evaporation, the strong complexation reactions with oxalic acid have the potential to increase the solubility of the actinides and generate higher losses during oxalate precipitation. During the scouting experiments used to develop the methodology to measure the specific volume of the oxalate slurry, the concentrations of all elements in the simulated solution were initially increased (simulating evaporation) to generate a larger, more easily measured volume of precipitate. Elemental analyses of the oxalate precipitation supernate (see Table 12) showed an increasing solubility of the lanthanide elements with increasing concentration of the metal impurities. The same effect on the Am/Cm solubility would also be expected. This observation is illustrated on Figure 8 by plotting lanthanide solubility as a function of the iron concentration. A complete curve for samarium was not generated since the concentration at low iron was below the ICP-ES detection limits. However, the data at higher iron concentrations indicate the curve would fall between praseodymium and europium. Comparison of Figure 8 with the lanthanide solubility curves (Figure 4) shows the order of the curves are generally the same. The crossover of the neodymium curve is more pronounced on Figure 8, presumably due to the high degree of complexation and the resulting decrease in the effective excess oxalic acid concentration. It also appears some time is required for the system to reach equilibrium due to competition between oxalate complexation and lanthanide precipitation. In experiment ACP-12, which contained the highest impurity concentrations, additional material precipitated in the graduated cylinder used to perform the experiment and supernate samples while the solutions were stored overnight.

Supernate Wash Model

Since the metal impurities in the Tank 17.1 solution will remain almost completely soluble after the addition of oxalic acid, a large fraction of the unwanted material can be removed by decanting followed by a series of oxalic/nitric acid washes. The measured concentration of these

elements as a function of 5 sequential 0.25M oxalic acid/0.5M nitric acid washes is shown for experiments ACP-6, ACP-7, ACP-8, and ACP-10 in Table 6-8, and 10, respectively. The measured concentrations closely agree with the concentrations calculated from a supernate wash model (see equation (1)) derived from a generalized material balance which assumes complete solubility.

$$C_{N_i} = Cs_i\left(\frac{V_S - V_R}{V_W - V_S - V_R}\right)^N \qquad (1)$$

where: C_{N_i} ≡ concentration of ith species after N wash cycles
Cs_i ≡ solubility of ith species in the supernate
V_S ≡ volume of supernate
V_R ≡ volume of supernate removed before the first wash
V_W ≡ volume of wash solution

The model also assumes the volume of wash solution (V_W) and the volume of solution removed after each wash are equal and the volume is the same for all wash cycles.

For illustration purposes, the measured and predicted concentration of iron, aluminum, and sodium (the most abundant metal impurities in Tank 17.1) are plotted as a function of the wash number on Figures 9-11. The predicted values are shown as a continuous line for clarity. Equation (1) may also be used to calculate the concentration of uranium as a function of the number of wash cycles given the concentration in the oxalate precipitation supernate.

Dissolved Melter Feed

The concentrations of the lanthanides and metal impurities in the dissolved melter feed were calculated by accounting for dilution after the 250 ml aliquot of concentrated (15.7M) nitric acid was added to dissolve the precipitate slurry remaining after the fifth wash cycle (see Tables 6-8 and 10). The lanthanide concentrations were calculated by using the concentrations in the simulated solution and assuming no losses. The percent recovery was then calculated from the ratio of the analyzed to the calculated concentration. Except for lanthanum, the recovery of the lanthanide elements was greater than 95% for excess oxalic acid concentrations of 0.3M or greater. From the low solubilities of Am/Cm (see Figures 5 and 6), one would also expect theoretical recoveries approaching 100%.

The concentrations of the metal impurities predicted from equation (1) after the fifth wash cycle were used to calculate the melter feed concentrations given in Tables 6-8 and 10. Good agreement between the calculated and measured concentrations provide confirmation that these elements are almost completely soluble under the conditions investigated.

Properties of Precipitate Slurry

Initially, three small-scale scouting experiments were performed to gain experience and develop the methodology required to make an accurate measurement of the specific volume of the oxalate slurry. The experiments were designed based on the measured specific volume of the simulated Am/Cm surrogate (3.6 liters/mole of simulant) reported by Gray et al.[1] and the use of the 120-mm diameter glass precipitator. The concentrations of all elements in the simulated solution were initially increased (simulating evaporation) to generate a larger, more easily measured volume of precipitate. The simulated solutions were prepared to generate 6 (ACP-11) and 9-inch (ACP-12 and ACP-13) slurry layers on the bottom of the large precipitator. The specific volumes measured during these experiments ranged between 0.5 and 0.7 liters/mole of lanthanides, compared to the previously reported value of 3.6. The large difference in specific volumes is likely due to a high concentration and subsequent precipitation of sodium from the simulated solution used by the previous investigators. The results from the small-scale experiments are summarized in Table 13.

Once the deleterious effect of high concentrations of aluminum and transition metal impurities on the oxalate precipitation were seen and resolved in experiment ACP-13, a large-scale precipitation was performed using the 120-mm diameter glass precipitator. The target concentrations of the simulated solution for this experiment (ACP-14) were the same as prepared for experiment ACP-13. The concentrations of the metal impurities in the simulant were held at approximately the same concentrations as in Tank 17.1 while the lanthanide concentrations were increased by a factor of approximately 8.5. Using this solution, the specific volume of the oxalate precipitate slurry was found to be 0.5 liters per mole of lanthanide/actinide simulant. The precipitations were performed at 60°C using a 0.9M solution of oxalic acid. The excess oxalic acid concentration was adjusted to 0.3M. The results of the specific volume measurement and elemental concentrations in the precipitation supernate are summarized in Tables 13 and 14, respectively.

When the precipitator stirrer was stopped, most of the precipitate settled in a few minutes. The supernate was clear of all but the smallest particles after 30 minutes. Typical particle settling rates observed were on the order of 30 cm/min. The build-up of precipitate on the top edge of the stirrer blades also demonstrated that the precipitate will settle on any horizontal surfaces in a canyon tank such as cooling coils and agitator blades. This has the potential to lead to high Am/Cm losses during in-tank processing when solution is removed from the tank.

It should also be noted that the settling behavior of the simulated oxalate precipitate may not be entirely typical of the settling rate in Tank 17.1. The presence of high alpha radiation (primarily from curium-244) in the tank may have an effect on the settling rate. Alpha radiation will cause the breakup of curium-containing particles, possible creating fines that do not settle as rapidly as most of the oxalates seen in the simulated precipitation. The slow settling fines may be a better model for the curium oxalate.

Once the precipitate settles to the bottom of the tank, the suction from the steam jet should not disturb the precipitate. A dip tube placed 1-inch from the top of the oxalate slurry did not disturb the precipitate during removal of supernate from the precipitator. The measured velocity of the solution through the tube, based on volume and time, was approximately 560 ft/min. This value is well above the maximum velocity of typical canyon steam jets. F-Canyon normally uses two standard jets for solution transfers: a 75 gal/min jet with a linear face velocity of 460 ft/min and a 25 gal/min jet with a linear face velocity of 155 ft/min.[1]

Conclusions and Recommendations

The small-scale experiments demonstrated that uranium and metal impurities in Tank 17.1 will remain soluble during in-tank processing. The majority of the lanthanides and plutonium and essentially all of the Am/Cm will be isolated as a precipitate slurry during the oxalate precipitation. Optimal precipitation conditions include adjusting the nitric acid concentration to less than 1M, heating the solution to 60°C, adding the oxalic acid precipitate (over a 15 to 30 minute period with agitation) until an excess of 0.3M is reached, and holding the solution at 45°C during a 4 hour digestion period. Although, the majority of the precipitate settled in only a few minutes during the laboratory experiments, a minimum of 8 hours should be used during processing of the Tank 17.1 material to insure complete settling of potential curium oxalate fines. The solution temperature should not exceed 35°C during the settling period (and subsequent wash cycles).

Once the precipitation is complete, unwanted, soluble materials, such as uranium, iron, aluminum, and sodium can be removed by decanting and a series of 0.25M oxalic acid/0.5M nitric acid washes. The amount of impurities removed during the wash are only functions of the volume and number of wash cycles. Larger volumes of oxalic acid or wash solution will reduce the number of wash cycles required to achieve a specified separation. The removal of specific elements during the precipitation and wash cycles can be predicted by assuming complete solubility and taking into account the dilution provided by the oxalic acid precipitate or wash solution.

Although the concentration of the actinides in Tank 17.1 are dilute, significant evaporation of the solution should not be attempted. Higher concentrations of the soluble elements such as iron aluminum, and uranium which form strong oxalate complexes, will increase the solubility of the Am/Cm by reducing the effective excess free oxalate concentration. Compensation for a high degree of complexation can be provided by adding additional oxalic acid during the precipitation; however, the exact requirements would require additional development work to define the optimal concentration and measurement of the new precipitate slurry properties.

Using approximately 2 liters of simulated Tank 17.1 solution, the specific volume of the oxalate slurry was found to be 0.5 liters per mole of lanthanide/actinide simulant. When the precipitator stirrer was stopped, most of the precipitate settled in only a few minutes. The supernate was

clear of all but the smallest particles after 30 minutes. The experiment also demonstrated that the precipitate will settle on any horizontal surfaces in a canyon tank such as cooling coils and agitator blades. However, once settled to the bottom of the tank, the suction from a steam jet should not disturb the precipitate. A dip tube placed 1-inch from the top of the oxalate slurry did not disturb the precipitate during removal of supernate from the precipitator. The measured velocity of the solution was well above the maximum velocity of typical canyon steam jets.

During the original separation of the Am/Cm contained in Tank 17.1 from the aluminum nitrate-containing waste solution, the decanting losses were much higher than anticipated. A total of about 20% of the product was entrained to the waste evaporator with the decanted supernate. The high losses were attributed to the solids, particularly those settled on the coils and agitator blades, being disturbed prior to and during the transfer of solution. A new decant jet, with a plate welded across the bottom and holes drilled around the pipe above the plate to provide horizontal rather than vertical suction, was used without success to lower the transfer losses.[7] From this information, it appears the transfer losses can be reduced by minimizing the number of supernate transfers. This can be accomplished by reducing the concentration of the oxalic acid precipitant and using a larger volume to adjust the excess concentration to 0.3M. The larger volume of solution will allow more of the uranium and metal impurities to be removed during the supernate transfer. Performing the precipitation in this manner coupled with the use of the maximum volume of wash solution (which can be accommodated by the processing tank) will minimize the number of wash cycles and solution transfers required to achieve a specified separation.

Alternately, a process strategy could be developed to perform the in-tank precipitation and subsequent washes without bringing the solution level below the coils or agitator blades. If the tip of the transfer jet is above the coils, the potential for entrainment is minimized; however, the number of washes required to remove a sepecified amount of uranium and metal impurities increases. A solution level between 4 and 5 feet would be required in an 8-ft (diameter) X 11-ft (tall) tank to cover the coils. This would leave between 50 and 60% of the working volume available for the wash solution.

If turbulence in the tank and entrainment of solids due to the steam jet operation is the principal cause of Am/Cm losses, alternatives to steam jets for solution transfer exist. Air lifts have been used successfully in the canyons for frame operation to transfer solution from tanks to ion exchange columns. Flow rates in the range of 10 gal/min are typical. This compares to 25 gal/min for a low flow steam jet. This provides another option for consideration if high losses of Am/Cm cannot be recycled or discarded to waste.

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Figure 1 Am/Cm Purification in F-Canyon

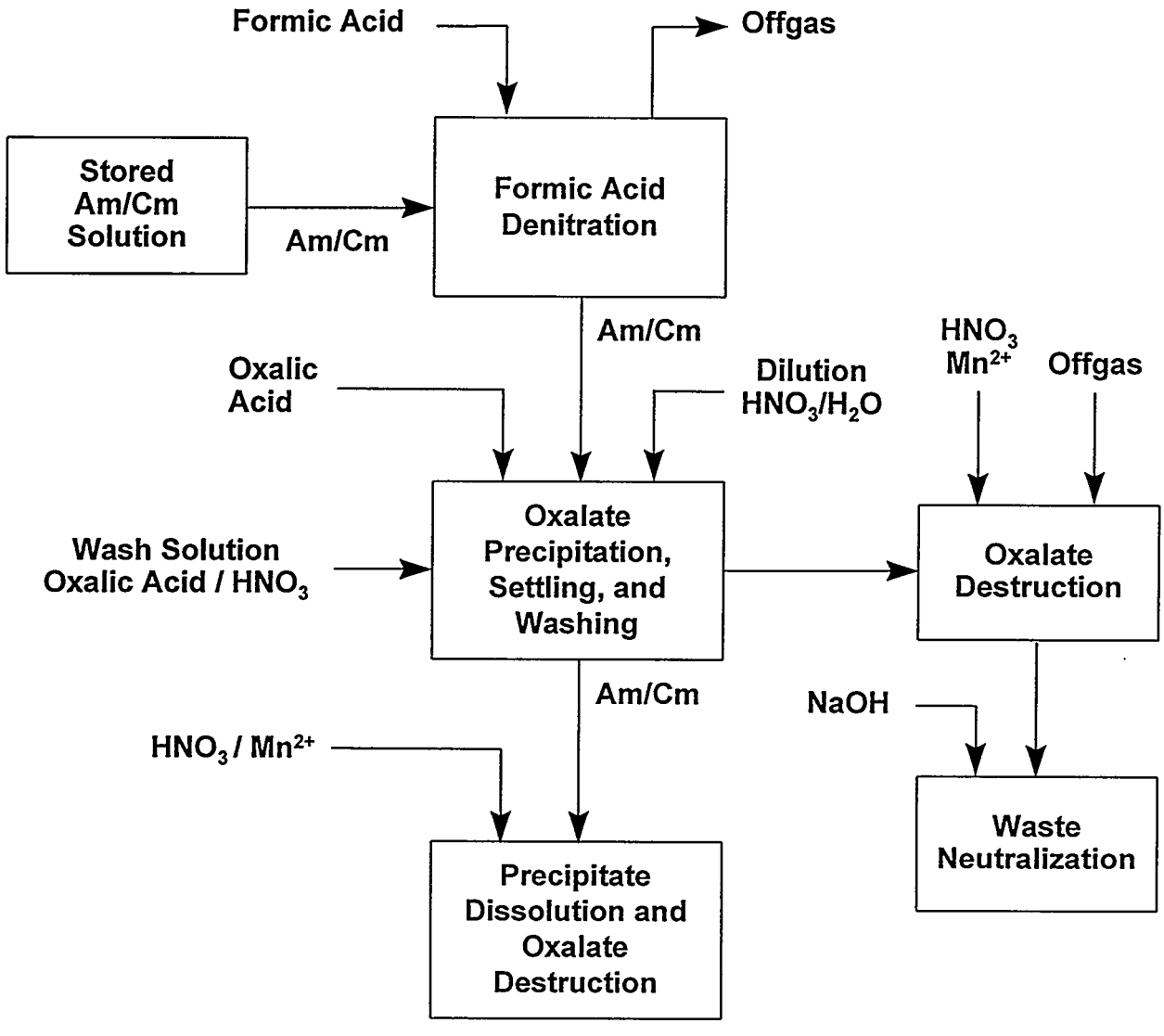
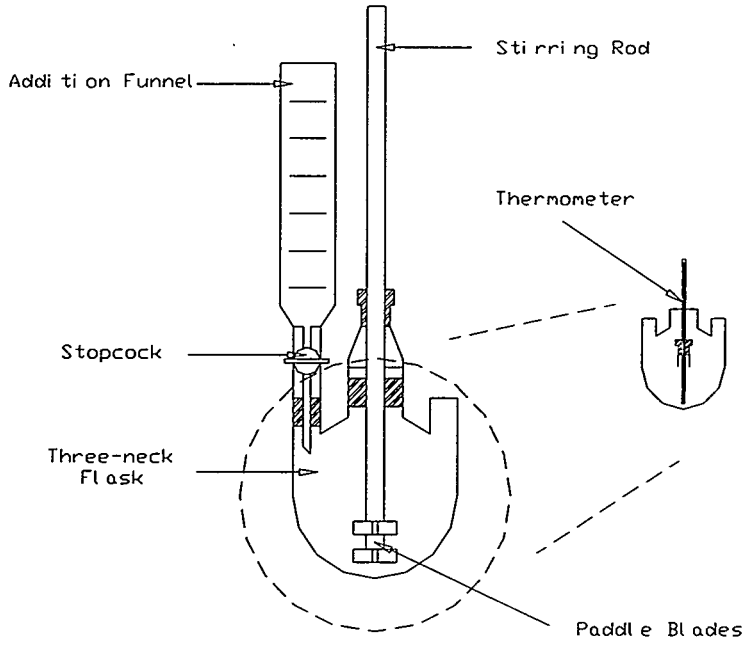
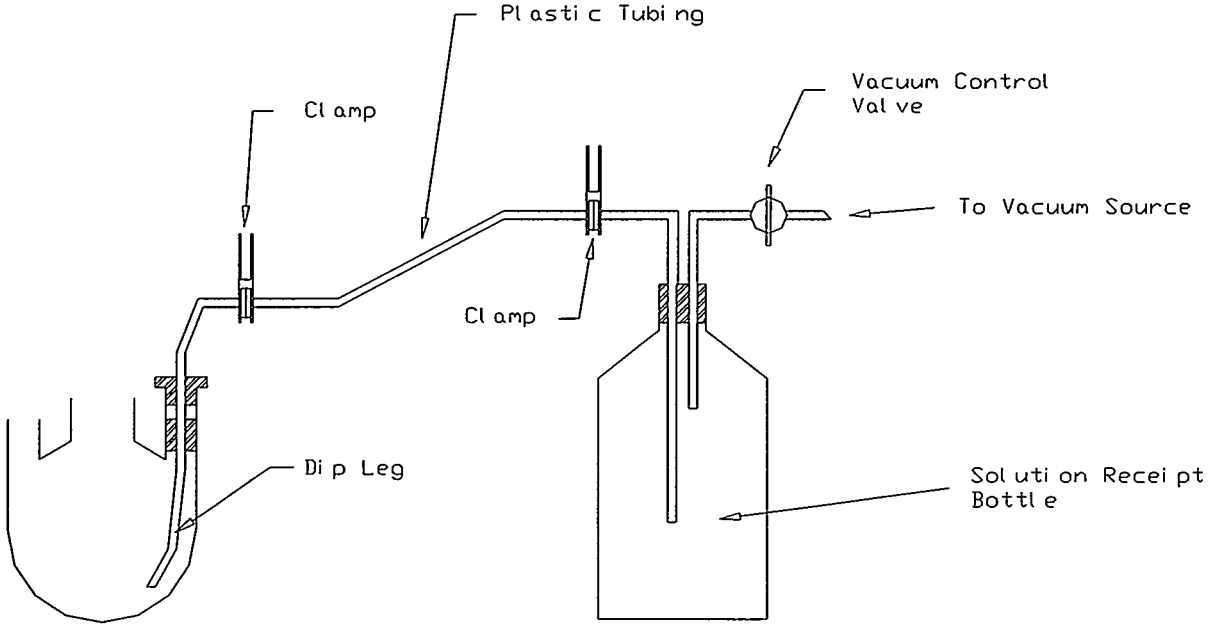


Figure 2 Small-scale Precipitation Equipment

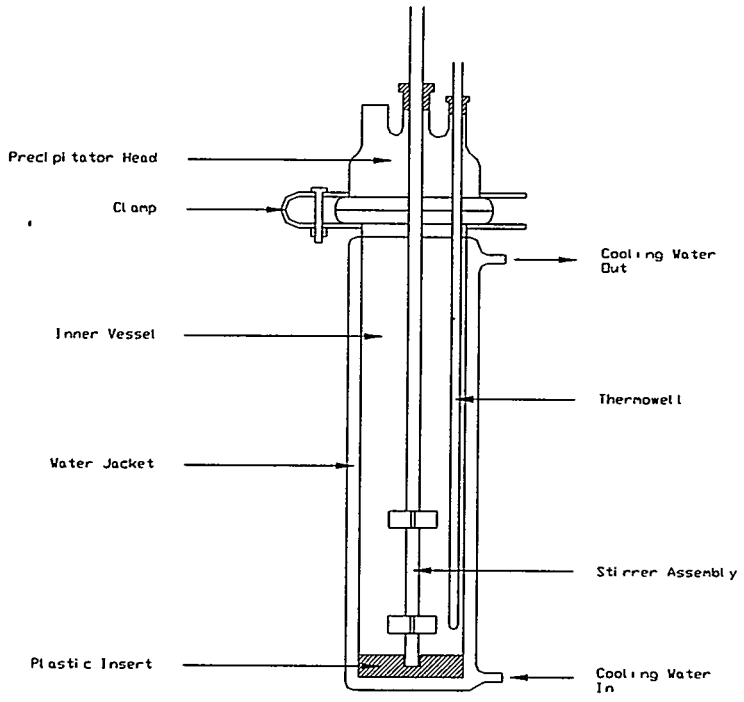


Precipitation Vessel

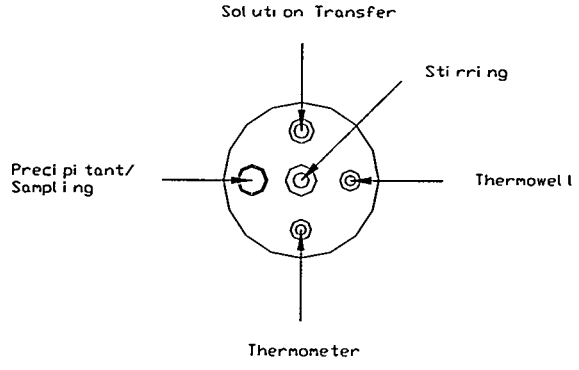


Solution Transfer Equipment

Figure 3 Large-scale Precipitation Equipment



Precipitator



Precipitator Head

Figure 4 Solubility of Lanthanide Oxalates

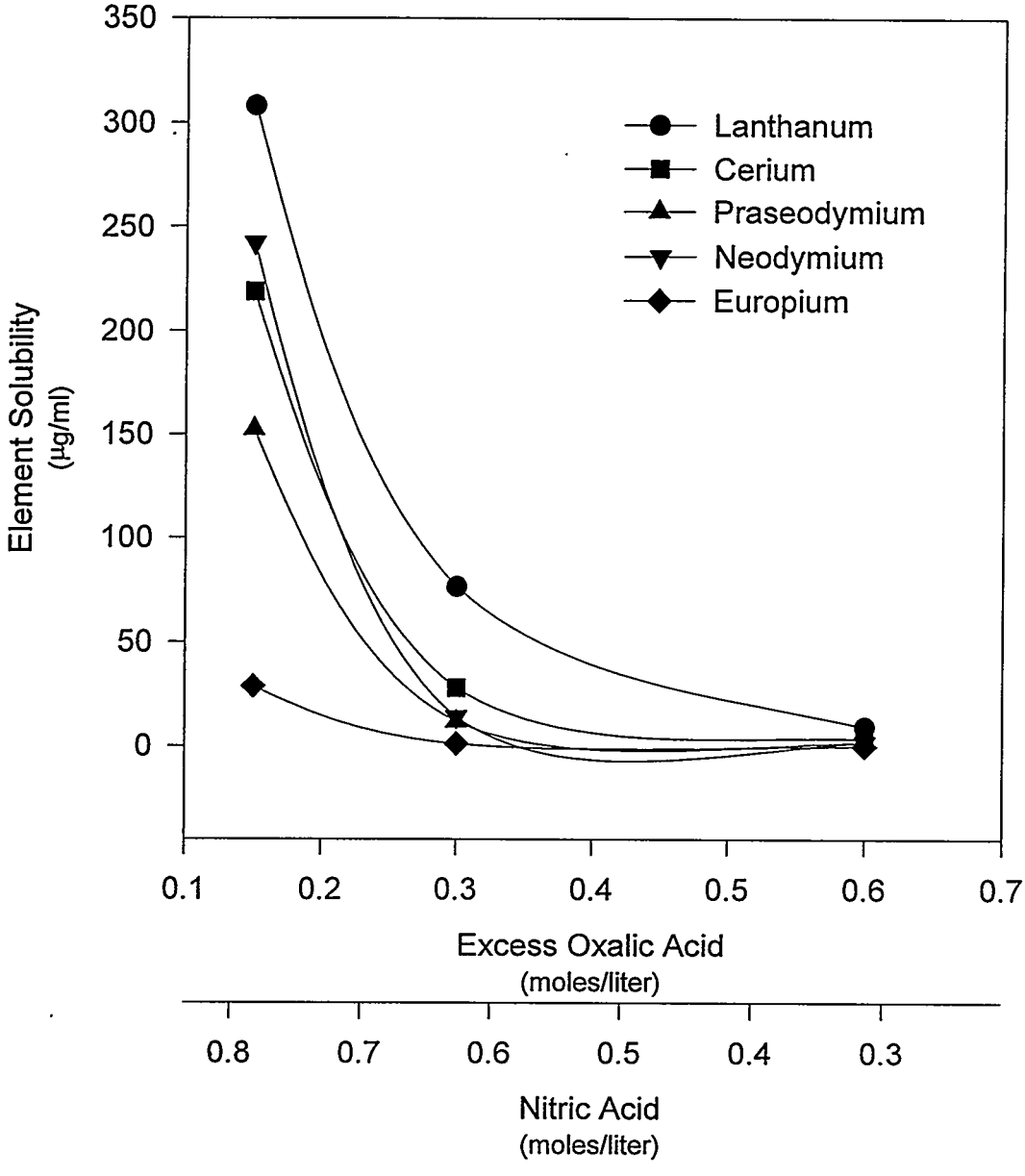


Figure 5 Solubility of Americium (III) Oxalate[5]

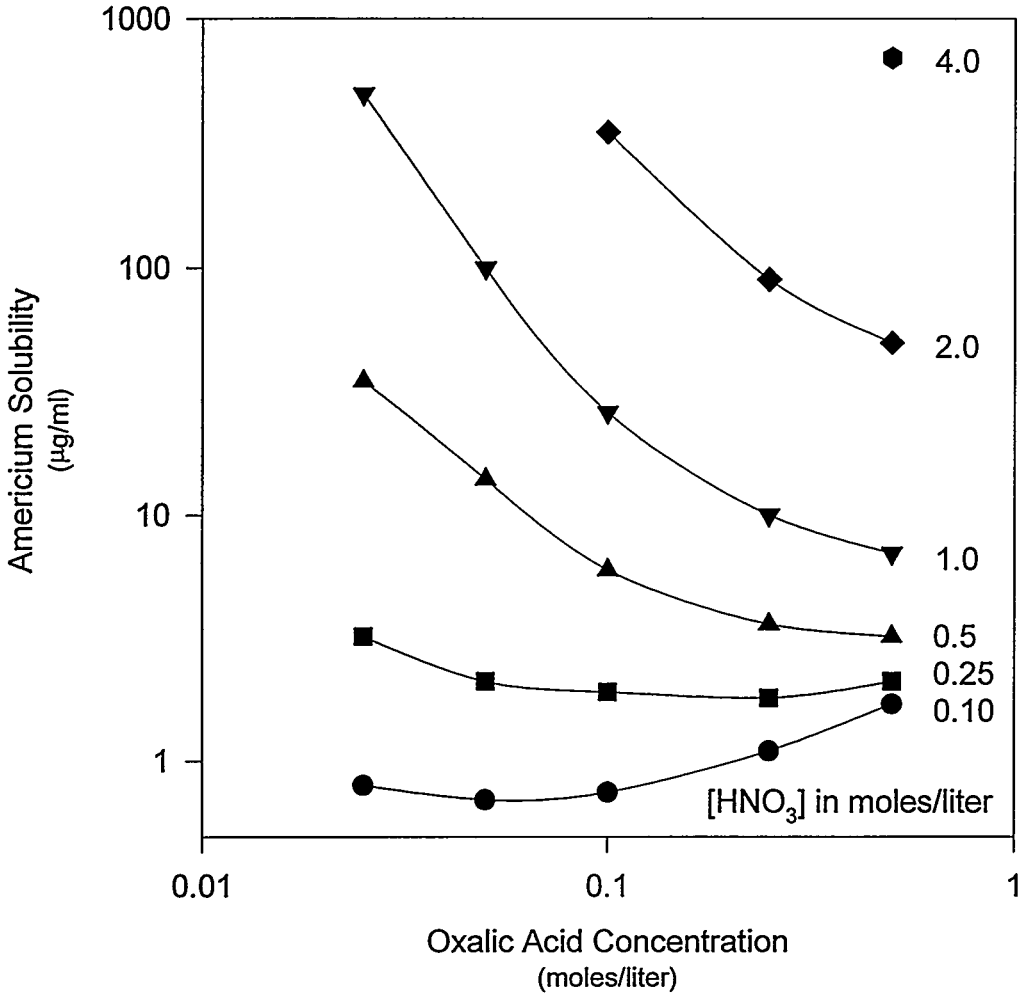


Figure 6 Solubility of Curium (III) Oxalate[5]

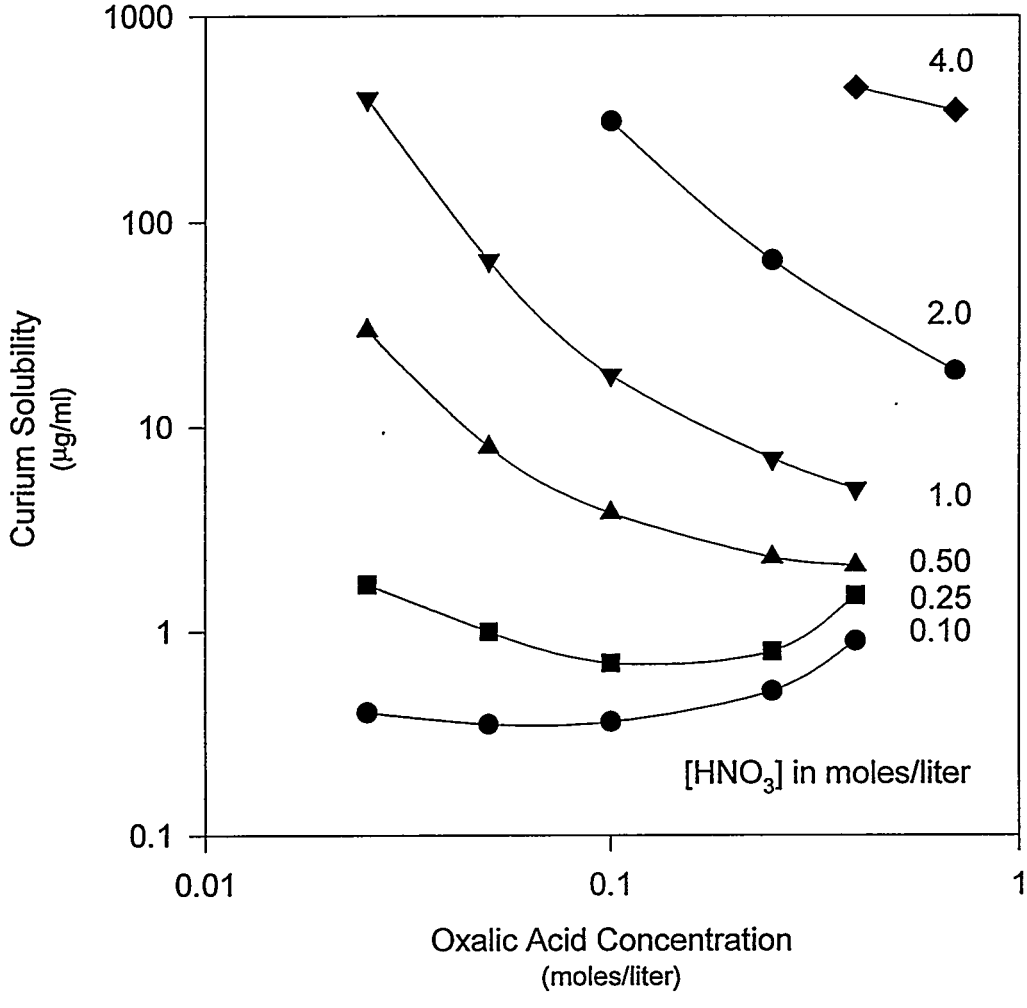


Figure 7 Solubility of Plutonium (IV) Oxalate[5]

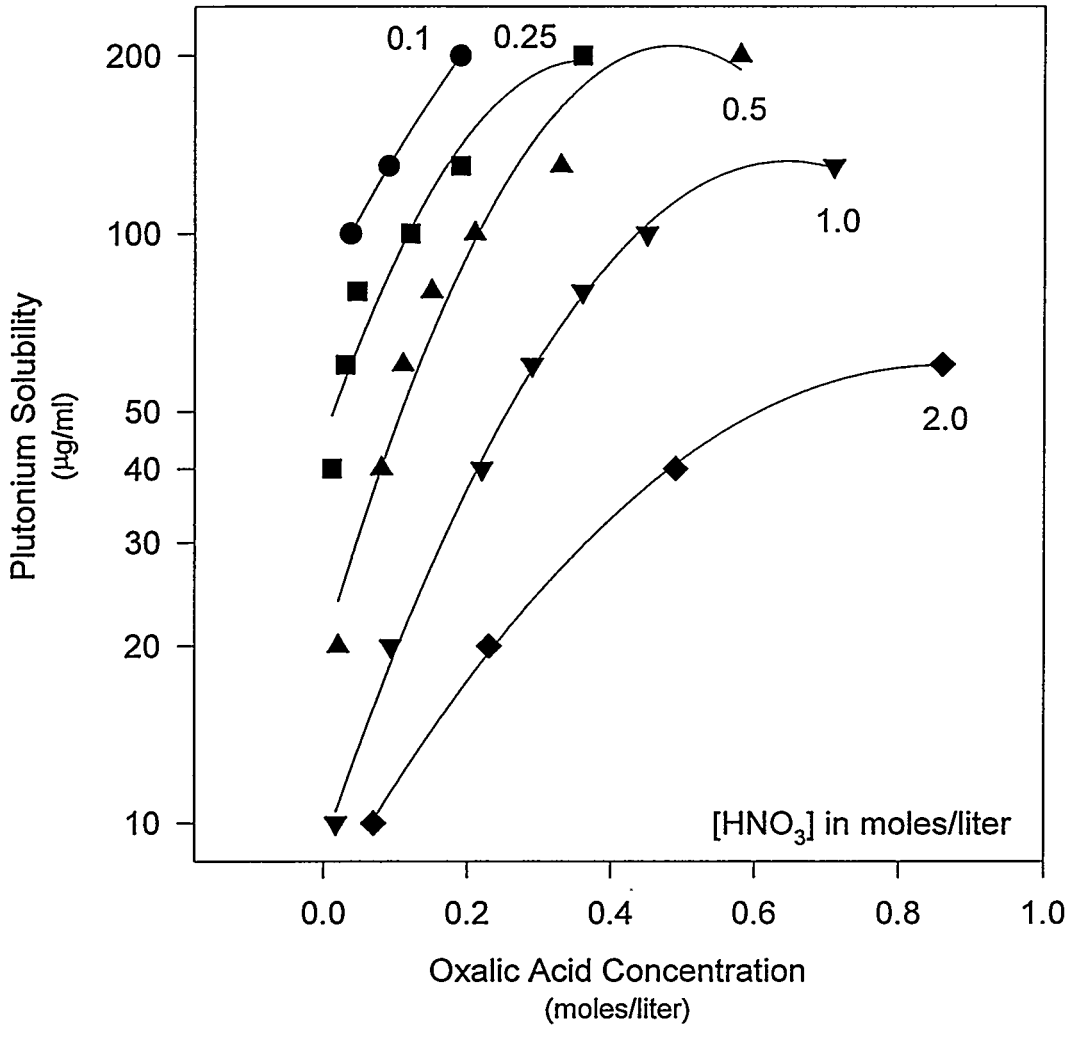


Figure 8 Effect of Iron on the Solubility of Lanthanide Oxalates

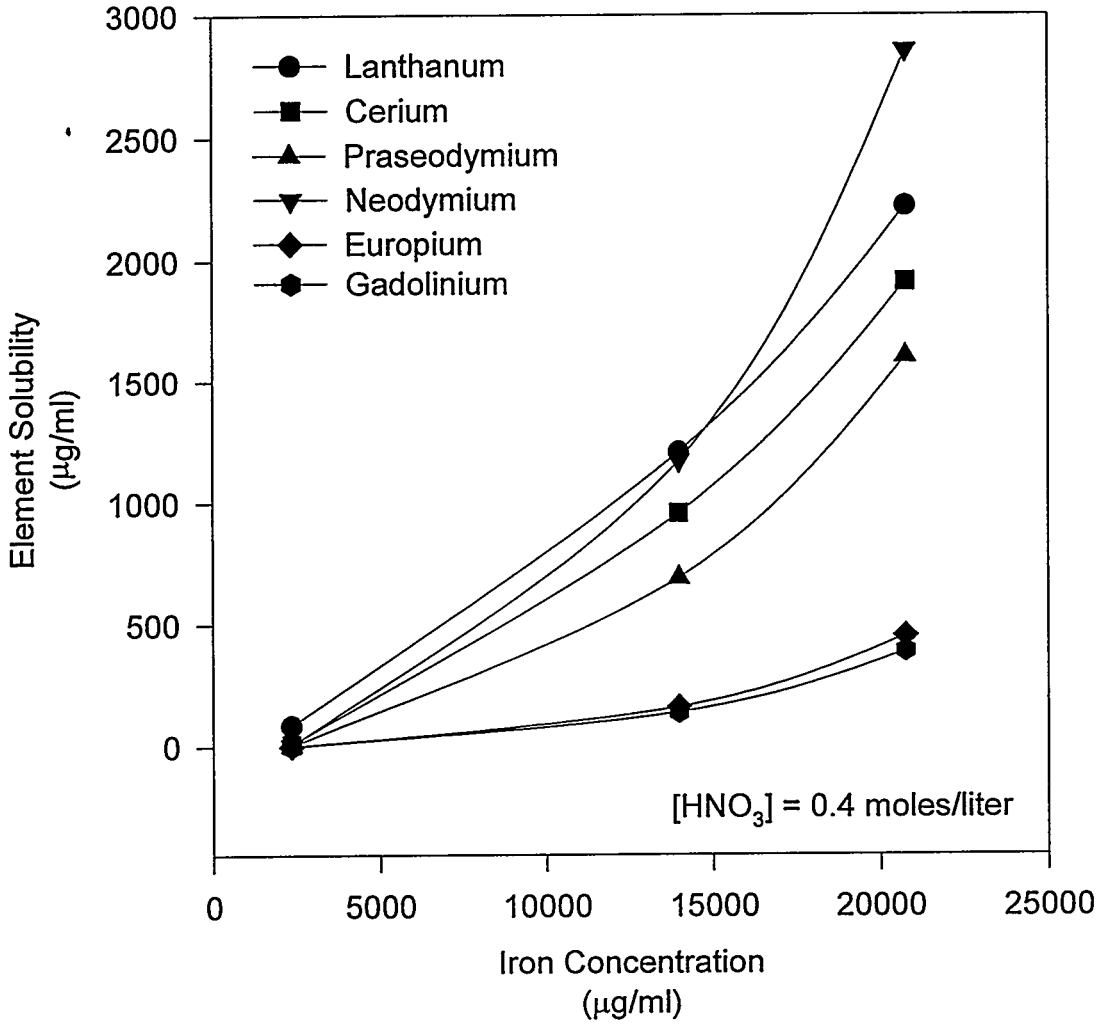


Figure 9 Removal of Iron from Oxalate Precipitation Supernate

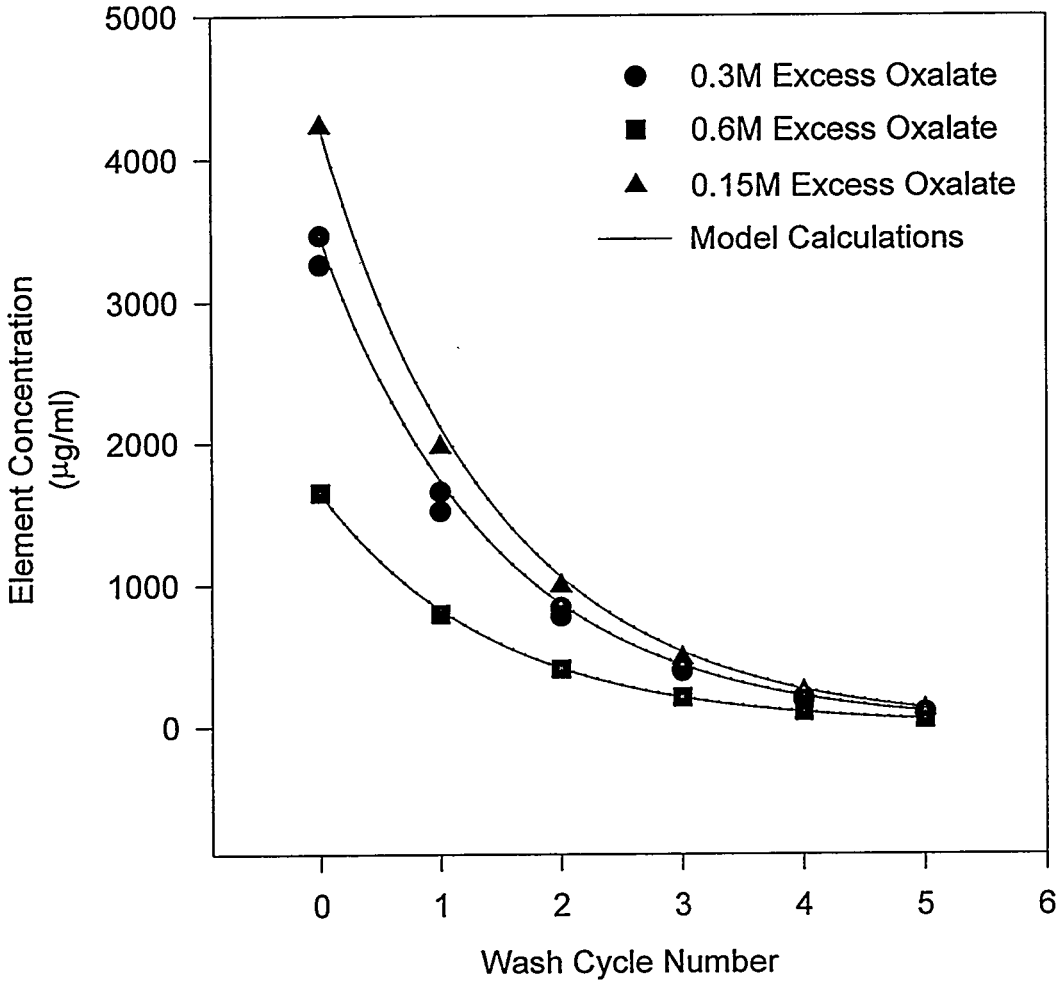


Figure 10 Removal of Aluminum from Oxalate Precipitation Supernate

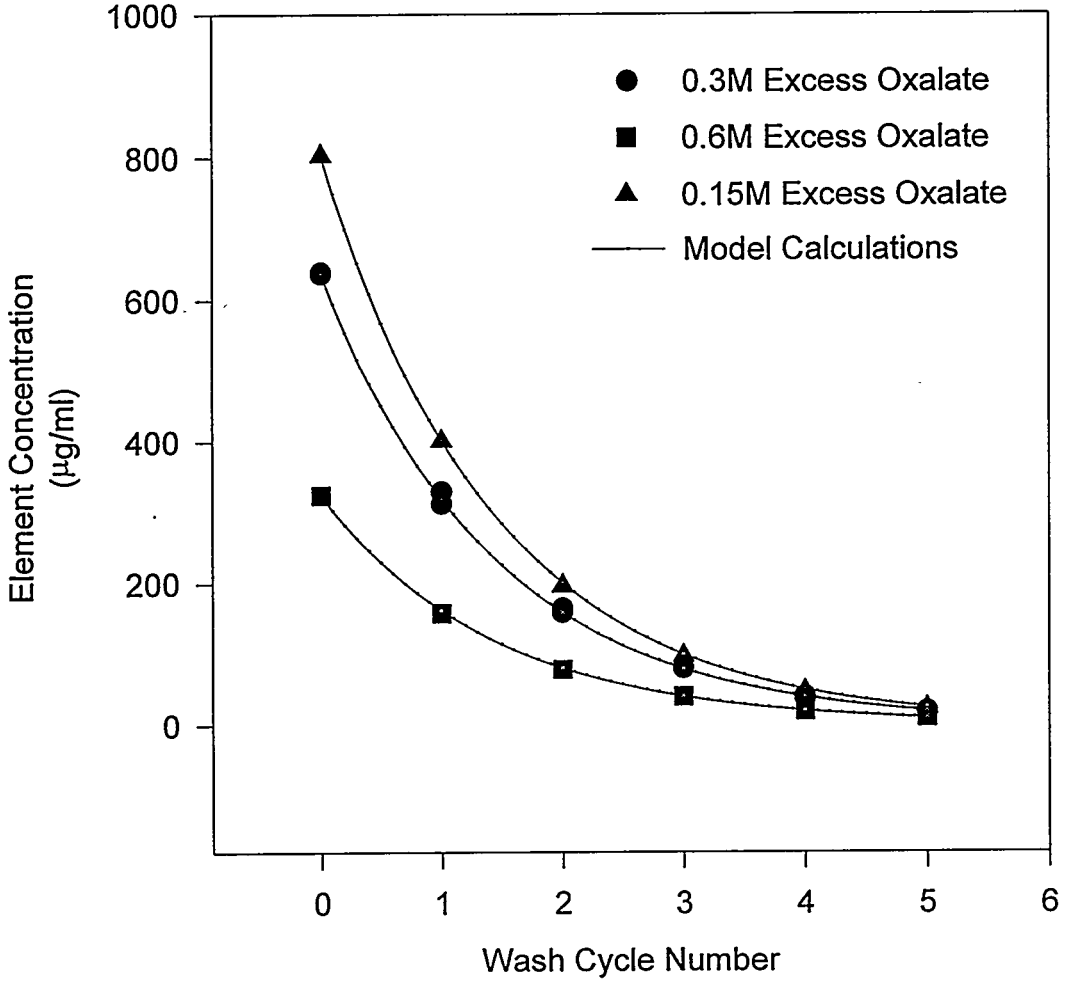


Figure 11 Removal of Sodium from Oxalate Precipitation Supernate

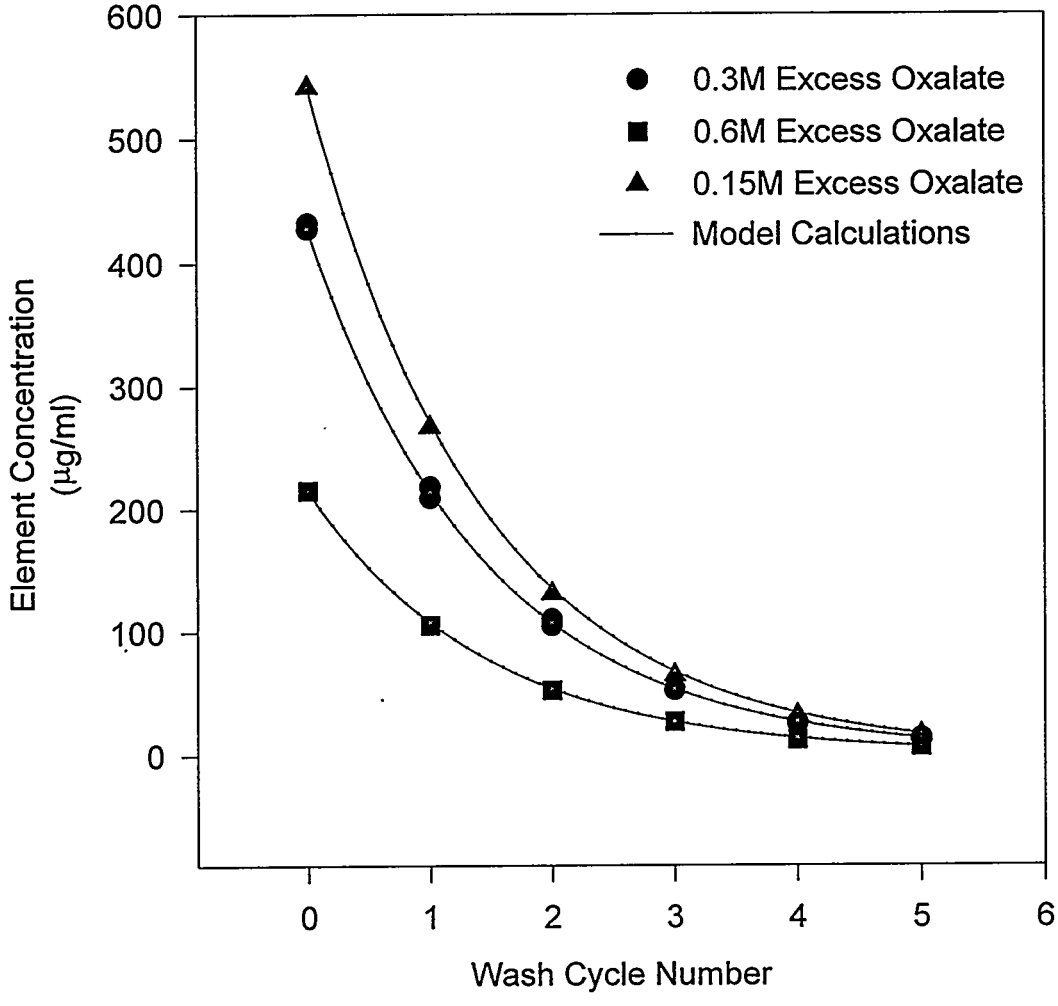


Table 1 Chemical Analysis of Tank 17.1 Solution

Lanthanides and Miscellaneous Metals

Lanthanides	Grams	Element	Grams
La	10,598	Al	16,200
Ce	12,112	B	154
Pr	12,112	Ca	999
Nd	25,738	Cr	4,330
Sm	6,056	Fe	74,943
Eu	1,211	K	<3255
Gd	3,028	Mn	3,588
Tb	<454	Na	10,174
Dy	<454	Ni	3,452
Ho	<454	Si	273
Er	<454	Zn	318
Tm	<606	Zr	61
Yb	<454		
Lu	<454		

Actinides

Element	Grams	Isotope	Wt. %
Total U	9387	U-234	0.204
		U-235	0.198
		U-236	0.037
		U-238	99.562
Total Pu	2471	Pu-238	5.832
		Pu-239	2.494
		Pu-240	86.636
		Pu-241	0.058
		Pu-242	4.981
Total Am	10159	Am-241	4.51
		Am-242m	0.02
		Am-243	95.47
Total Cm	2740	Cm-244	93.27
		Cm-245	3.57
		Cm-246	3.11
		Cm-247	0.05

Table 2 Operating Limits for Am/Cm Purification in F-Canyon

Denitration	Min	Max	Units
Evaporator Solution			
1. Volume	2400	4700	liters
2. Temperature	90	(a)	°C
3. HNO_3 Concentration	0.2	10.0	M
Formic Acid Feed			
1. Formic Acid Concentration	88	92	Wt%
2. Quantity of Formic Acid Added	1.00	1.55	(b)
3. Addition Rate	0.5	3.2	lb/min
4. Temperature in Storage	0	60	°C
Precipitation			
Oxalic Acid Feed Make-up			
1. Oxalic Acid Concentration	0.8	1.0	M
2. Temperature in Storage	20	80	°C
Oxalic Acid Addition			
1. Precipitator Solution Temperature	60	80	°C
2. HNO_3 Concentration (c)	-	0.20	M
Aluminum Concentration	-	0.5	M
Sodium Concentration	-	0.5	M
Digestion			
1. Solution Temperature	40	47	°C
2. Time	4	-	hours
Settling			
1. Solution Temperature	-	35	°C
2. Time	8	-	hours
Oxalate Oxidation			
1. Manganous Ion Concentration	-	0.02	M
2. HNO_3 Concentration	1	5	M

(a) Boiling Point is Limiting
(b) Moles of Formic Acid per Mole of HNO_3 Consumed
(c) After Oxalic Acid Addition is Completed

Table 3 Uranium Oxalate Solubility Data

Exp't		U Simulant (μg/ml)	La Simulant (μg/ml)	U Supernate (μg/ml)	U Calc (μg/ml)	La Supernate (μg/ml)	$H_2C_2O_4$ Calc (moles/l)	HNO_3 Calc (moles/l)
ACP-1	Average	567		360	378		0.30	0.67
	95% CL	20		37	13			
ACP-2	Average	567		185	189		0.60	0.33
	95% CL	20		9	7			
ACP-3	Average	563	5117	288	299	11	0.39	0.53
	95% CL	18	75	8	9	3		
ACP-4	Average	563	5117	330	352	27	0.30	0.63
	95% CL	18	75	43	11	2		
ACP-5	Average	563	5117	340	352	25	0.30	0.63
	95% CL	18	75	13	11	1		

Table 4 Comparison of Measured and Calculated Uranium Concentrations

Exp't	U Supernate (µg/ml)	S_U Supernate (µg/ml)	U Calc (µg/ml)	S_U Calc (µg/ml)	S_{pooled} (µg/ml)	t_{calc}	Degrees Freedom	$t_{0.025}$
ACP-1	360	35	378	14	26	0.699	11	2.201
ACP-2	185	6	189	7	7	0.599	9	2.262
ACP-3	288	5	299	14	13	0.879	13	2.160
ACP-4	330	27	352	16	19	1.151	13	2.160
ACP-5	340	8	352	16	15	0.825	13	2.160

Table 5 Precipitation Conditions for Am/Cm Pretreatment Experiments

Experiment	Final Precipitation Conditions		No. Wash Cycles
	$H_2C_2O_4$ (moles/l)	HNO_3 (moles/l)	
ACP-6	0.30	0.63	5
ACP-7	0.60	0.31	5
ACP-8	0.15	0.78	5
ACP-9	0.30	0.63	0 (a)
ACP-10	0.30	0.63	5

(a) The oxalate precipitate was not washed due to problems with the stirrer operation.

Table 6 Oxalate Solubility Data for Experiment ACP-6

Lanthanides

	La (µg/ml)	Ce (µg/ml)	Pr (µg/ml)	Nd (µg/ml)	Sm (µg/ml)	Eu (µg/ml)	Gd (µg/ml)
Simulant							
Makeup	700	807	802	1700	502	500	321
Analysis	712	775	797	1674	522	374	312
Supernate							
Analysis	75.6	25.4	10.3	13.1	<2.500	1.4	1.0
1st Wash							
Analysis	30.6	7.1	2.6	<2.000	<2.500	0.2	<0.370
2nd Wash							
Analysis	14.4	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
3rd Wash							
Analysis	7.1	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
4th Wash							
Analysis	4.4	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
5th Wash							
Analysis	3.2	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
Feed							
Analysis	304	382	396	830	263	186	158
Calc (a)	365	397	408	857	267	191	160
Recovery	83%	96%	97%	97%	98%	97%	99%

(a) Volume of solution after fifth wash was 0.238 liters

Table 6 Continued

Metal Impurities

	Al (µg/ml)	Ca (µg/ml)	Fe (µg/ml)	K (µg/ml)	Mn (µg/ml)	Na (µg/ml)	Ni (µg/ml)
Simulant							
Makeup	1071	66	4955	215	237	673	229
Analysis	1002	65	5322	205	224	682	215
Supernate							
Analysis	637	40.5	3465	131	145	428	140
Predict	624	40.6	3326	128	140	426	134
1st Wash							
Analysis	329	21.0	1654	65.5	74.2	218	72.4
Model	319	20.2	1732	65.6	72.3	214	70.1
2nd Wash							
Analysis	165	10.6	838	34.5	37.5	110	36.1
Model	159	10.1	866	32.8	36.2	107	35.0
3rd Wash							
Analysis	81.1	5.7	399	16.9	18.6	53.3	17.5
Model	79.7	5.1	433	16.4	18.1	53.5	17.5
4th Wash							
Analysis	40.2	3.2	206	7.6	9.1	26.1	8.8
Model	39.8	2.5	217	8.2	9.0	26.8	8.8
5th Wash							
Analysis	19.4	1.7	100	4.1	4.6	13.1	4.4
Model	19.9	1.3	108	4.1	4.5	13.4	4.4
Feed							
Analysis	13.5	2.6	51.0	2.1	2.4	6.8	2.8
Calc (a)	9.7	0.6	52.8	2.0	2.2	6.5	2.1

(a) Volume of solution after fifth wash was 0.238 liters

Table 7 Oxalate Solubility Data for Experiment ACP-7

Lanthanides

	La (µg/ml)	Ce (µg/ml)	Pr (µg/ml)	Nd (µg/ml)	Sm (µg/ml)	Eu (µg/ml)	Gd (µg/ml)
Simulant							
Makeup	700	807	802	1700	502	500	321
Analysis	712	775	797	1674	522	374	312
Supernate							
Analysis	9.5	<2.800	<1.100	<2.000	<2.500	0.2	<0.370
1st Wash							
Analysis	5.2	<2.800	<1.100	<2.000	<2.500	0.1	<0.370
2nd Wash							
Analysis	3.8	<2.800	<1.100	<2.000	<2.500	0.1	<0.370
3rd Wash							
Analysis	3.2	<2.800	<1.100	<2.000	<2.500	0.1	<0.370
4th Wash							
Analysis	2.6	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
5th Wash							
Analysis	2.4	<2.800	<1.100	<2.000	<2.500	0.1	<0.370
Feed							
Analysis	356	385	421	863	277	195	167
Calc (a)	364	396	408	856	267	191	160
Recovery	98%	97%	103%	101%	104%	102%	104%

(a) Volume of solution after fifth wash was 0.239 liters

Table 7 Continued

Metal Impurities

	Al (µg/ml)	Ca (µg/ml)	Fe (µg/ml)	K (µg/ml)	Mn (µg/ml)	Na (µg/ml)	Ni (µg/ml)
Simulant							
Makeup	1071	66.0	4955	215	237	673	229
Analysis	999	65.4	5405	202	221	675	212
Supernate							
Analysis	324	20.9	1648	66.6	76.4	215	74.2
Predict	314	20.6	1700	63.5	69.5	212	66.7
1st Wash							
Analysis	158	10.9	794	32.6	37.1	105	36.1
Model	162	10.5	824	33.3	38.2	108	37.1
2nd Wash							
Analysis	78.7	5.9	404	15.7	18.5	52.2	18.1
Model	81.0	5.2	412	16.6	19.1	53.8	18.5
3rd Wash							
Analysis	40.1	2.8	205	7.5	9.5	26.7	9.3
Model	40.5	2.6	206	8.3	9.5	26.9	9.3
4th Wash							
Analysis	19.3	1.9	102	3.8	4.5	12.0	4.4
Model	20.3	1.3	103	4.2	4.8	13.4	4.6
5th Wash							
Analysis	9.6	1.2	49.8	2.0	2.3	6.4	2.3
Model	10.1	0.7	51.5	2.1	2.4	6.7	2.3
Feed							
Analysis	9.0	3.2	27.3	1.0	1.5	4.2	2.6
Calc (a)	5.0	0.3	25.2	1.0	1.2	3.3	1.1

(a) Volume of solution after fifth wash was 0.239 liters

Table 8 Oxalate Solubility Data for Experiment ACP-8

Lanthanides

	La (µg/ml)	Ce (µg/ml)	Pr (µg/ml)	Nd (µg/ml)	Sm (µg/ml)	Eu (µg/ml)	Gd (µg/ml)
Simulant							
Makeup	700	807	802	1700	502	500	321
Analysis	712	775	797	1674	522	374	312
Supernate							
Analysis	308	219	153	242	48.6	29.0	27.9
1st Wash							
Analysis	57.7	20.5	8.3	8.4	<2.500	0.5	0.5
2nd Wash							
Analysis	20.8	4.8	1.7	<2.000	<2.500	<0.080	<0.370
3rd Wash							
Analysis	10.2	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
4th Wash							
Analysis	6.0	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
5th Wash							
Analysis	3.9	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
Feed							
Analysis	262	351	378	810	261	188	158
Calc (a)	357	389	400	840	262	188	157
Recovery	73%	90%	94%	96%	100%	100%	101%

(a) Volume of solution after fifth wash was 0.248 liters

Table 8 Continued

Metal Impurities

	Al (µg/ml)	Ca (µg/ml)	Fe (µg/ml)	K (µg/ml)	Mn (µg/ml)	Na (µg/ml)	Ni (µg/ml)
Simulant							
Makeup	1071	66.0	4955	215	237	673	229
Analysis	999	65.4	5405	202	221	675	212
Supernate							
Analysis	803	52.2	4227	172	185	542	178
Predict	783	51.3	4236	158	173	529	166
1st Wash							
Analysis	401	26.1	1971	86.2	92.3	267	88.7
Model	402	26.1	2113	86.1	92.3	271	88.9
2nd Wash							
Analysis	196	13.0	992	43.5	45.5	131	43.9
Model	201	13.1	1057	43.1	46.1	136	44.5
3rd Wash							
Analysis	97.6	6.6	480	19.3	22.3	64.3	21.5
Model	100	6.5	528	21.5	23.1	67.8	22.2
4th Wash							
Analysis	47.4	3.5	240	10.0	11.0	31.3	10.7
Model	50.2	3.3	264	10.8	11.5	33.9	11.1
5th Wash							
Analysis	23.1	1.9	115	4.7	5.3	15.6	5.2
Model	25.1	1.6	132	5.4	5.8	16.9	5.6
Feed							
Analysis	9.9	1.9	56.3	2.4	2.7	8.4	3.0
Calc	12.5	0.8	65.8	2.7	2.9	8.4	2.8

(a) Volume of solution after fifth wash was 0.248 liters

Table 9 Oxalate Solubility Data for Experiment ACP-9

Lanthanides

	La (μg/ml)	Ce (μg/ml)	Pr (μg/ml)	Nd (μg/ml)	Sm (μg/ml)	Eu (μg/ml)	Gd (μg/ml)
Simulant							
Makeup	700	807	802	1700	502	500	321
Analysis	712	775	797	1674	522	374	312
Supernate							
Analysis	77.4	29.1	12.3	14.0	<2.500	1.0	0.9

Metal Impurities

	Al (μg/ml)	Ca (μg/ml)	Fe (μg/ml)	K (μg/ml)	Mn (μg/ml)	Na (μg/ml)	Ni (μg/ml)
Simulant							
Makeup	1071	66.0	4955	215	237	673	229
Analysis	999	65.4	5405	202	221	675	212
Supernate							
Analysis	640	40.9	3234	127	146	433	138
Predict	624	40.9	3378	126	138	422	133

Table 10 Oxalate Solubility Data for Experiment ACP-10

Lanthanides

	La (µg/ml)	Ce (µg/ml)	Pr (µg/ml)	Nd (µg/ml)	Sm (µg/ml)	Eu (µg/ml)	Gd (µg/ml)
Simulant							
Makeup	700	807	802	1700	502	500	321
Analysis	712	775	797	1674	522	374	312
Supernate							
Analysis	77.2	30.2	13.5	15.6	<2.500	1.3	1.3
1st Wash							
Analysis	26.9	6.3	1.7	<2.000	<2.500	0.1	<0.370
2nd Wash							
Analysis	12.4	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
3rd Wash							
Analysis	6.6	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
4th Wash							
Analysis	3.9	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
5th Wash							
Analysis	2.6	<2.800	<1.100	<2.000	<2.500	<0.080	<0.370
Feed							
Analysis	310	385	403	854	268	190	162
Calc (a)	360	392	403	847	264	189	158
Recovery	86%	98%	100%	101%	101%	100%	102%

(a) Volume of solution after fifth wash was 0.244 liters

Table 10 Continued

Metal Impurities

	Al (µg/ml)	Ca (µg/ml)	Fe (µg/ml)	K (µg/ml)	Mn (µg/ml)	Na (µg/ml)	Ni (µg/ml)
Simulant							
Makeup	1071	66.0	4955	215	237	673	229
Analysis	999	65.4	5405	202	221	675	212
Supernate							
Analysis	639	51.3	3260	130	146	432	141
Predict	624	40.9	3378	126	138	422	133
1st Wash							
Analysis	312	22.4	1518	49.1	71.3	209	68.1
Model	319	25.7	1630	64.8	73.2	216	70.3
2nd Wash							
Analysis	159	10.7	778	32.5	36.4	105	34.9
Model	160	12.8	815	32.4	36.6	108	35.1
3rd Wash							
Analysis	80.4	8.7	390	15.4	18.3	52.8	17.4
Model	79.8	6.4	407	16.2	18.3	53.9	17.6
4th Wash							
Analysis	38.3	3.2	190	7.3	8.6	25.5	8.0
Model	39.9	3.2	204	8.1	9.2	27.0	8.8
5th Wash							
Analysis	19.4	1.7	94	3.9	4.4	12.5	4.0
Model	20.0	1.6	102	4.0	4.6	13.5	4.4
Feed							
Analysis	16.0	(a)	50.6	1.9	2.6	8.0	2.9
Calc (b)	9.9	0.8	50.3	2.0	2.3	6.7	2.2

(a) Not Available
(b) Volume of solution after fifth wash was 0.244 liters

Table 11 Selected Stability Constants for Oxalic Acid[6]

Metal Ion	Equilibrium	Log K 25°C, 0.1[a]	Log K 25°C, 1.0[a]	Log K 25°C, 0[a]
Al^{3+}	$ML/M \bullet L$		6.1	
	$ML_2/M \bullet L^2$		11.09	
	$ML_3/M \bullet L^3$		15.12	
Ca^{2+}	$ML/M \bullet L$		1.66	3.00[b]
	$ML_2/M \bullet L^2$		2.69	
Fe^{3+}	$ML/M \bullet L$	7.53[c] ± 0.1	7.59	7.74[d]
	$ML_2/M \bullet L^2$	13.64[c]		
	$ML_3/M \bullet L^3$	18.49[c]		
	$MHL/M \bullet HL$	4.35[c]		
K^+	$ML/M \bullet L$			-0.8[b]
Mn^{2+}	$ML/M \bullet L$	3.2		3.95±0.03
	$ML_2/M \bullet L^2$	4.4		
Ni^{2+}	$ML/M \bullet L$			5.16
UO_2^{2+}	$ML/M \bullet L$	6.36[e]	5.99[e]	
	$ML_2/M \bullet L^2$	10.59[e]	10.64[e]	
	$ML_3/M \bullet L^3$		11.0[e]	
Mn^{3+}	$ML/M \bullet L$		9.98[f]	
	$ML_2/M \bullet L^2$		16.57[f]	
	$ML_3/M \bullet L^3$		18.42[f]	

(a) Ionic Strength
(b) 18°C
(c) Ionic Strength equal to 0.5
(d) Ionic Strength equal to 3.0
(e) 20°C
(f) Ionic Strength equal to 2.0

Table 12 Solution Analysis for Precipitate Slurry Scouting Experiments

Exp't		Lanthanides						
		La (µg/ml)	Ce (µg/ml)	Pr (µg/ml)	Nd (µg/ml)	Sm (µg/ml)	Eu (µg/ml)	Gd (µg/ml)
ACP-11	Simulant							
	Makeup	4026	4760	4600	9835	2881	2912	1815
	Analysis	4157	4757	4605	9762	2996	2206	1792
	Supernate							
	Analysis	1207	956	689	1170	254	159	138
ACP-12	Simulant							
	Makeup	6125	6912	6903	14656	4437	4374	2756
	Analysis	6199	6893	6750	14217	4512	3235	2649
	Supernate							
	Analysis	2219	1911	1602	2853	726	452	388
ACP-13	Simulant							
	Makeup	6054	6989	6924	14670	4365	4050	2736
	Analysis	6406	7130	7159	14735	4719	3120	2753
	Supernate							
	Analysis	83.6	9.0	3.4	4.2	<2.500	0.8	0.6

Table 12 Continued

Metal Impurities

Exp't		Al (μg/ml)	Ca (μg/ml)	Fe (μg/ml)	K (μg/ml)	Mn (μg/ml)	Na (μg/ml)	Ni (μg/ml)
ACP-11	Simulant							
	Makeup	6173	377	28580	1253	1352	3871	1303
	Analysis	5930	379	30409	1186	1330	3961	1256
	Supernate							
	Analysis	2877	223	13976	575	660	1904	629
ACP-12	Simulant							
	Makeup	9315	570	42786	2047	2048	5801	1975
	Analysis	8804	581	44204	1923	1980	5894	1868
	Supernate							
	Analysis	4056	428	20754	872	928	2736	913
ACP-13	Simulant							
	Makeup	1068	66	4955	213	241	671	230
	Analysis	991	(a)	5386	207	236	711	231
	Supernate							
	Analysis	460	56.6	2345	94.3	109	315	104

(a) Analytical results were not available.

Table 13 Specific Volume of Oxalate Slurry

Experiment	Simulant Volume (liters)	Lanthanide (a) (moles)	Slurry Volume (liters)	Specific Volume (liters/mole)
ACP-11	0.209	0.044	0.02	0.5
ACP-12	0.212	0.065	0.03	0.5
ACP-13	0.212	0.068	0.05	0.7
ACP-14	1.960	0.656	0.3	0.5

(a) The moles of lanthanides are based on simulant concentrations given in Tables A.6-A.8.

Table 14 Oxalate Solubility Data for Experiment ACP-14

Lanthanides[a]

	La (µg/ml)	Ce (µg/ml)	Pr (µg/ml)	Nd (µg/ml)	Sm (µg/ml)	Eu (µg/ml)	Gd (µg/ml)
Simulant							
Makeup	6055	6909	6910	14686	4338	4318	2733
Analysis	6536	7248	7342	15146	4859	4377	2791
Supernate							
Analysis	86.4	7.8	2.0	2.7	<2.500	0.69	<0.370

Metal Impurities[a]

	Al (µg/ml)	Ca (µg/ml)	Fe (µg/ml)	K (µg/ml)	Mn (µg/ml)	Na (µg/ml)	Ni (µg/ml)
Simulant							
Makeup	1070	66	4950	216	237	671	228
Analysis	1034	(b)	5117	198	239	715	232
Supernate							
Analysis	440	30.4	2253	90.8	102	300	98.2
Predict	465	28.6	2151	94.0	103	292	98.9

(a) Supernate temperature was 35°C during sampling.
(b) Analytical results were not available.

Appendix A - Preparation of Simulated Solutions

Uranium Solubility Experiments

A 0.6 gram/liter (600 μg/ml) uranium solution was prepared by dissolving 1.3094 grams of depleted uranyl nitrate hexahydrate (UNH) in 1 liter of 1.0M nitric acid. The UNH was obtained from Mallinckrodt and assayed 100.6%. The concentrated nitric acid used to prepare the 1.0M solution was obtained from E. M. Science and assayed 69-71% (15.7M). The prepared and analyzed concentrations for the solution are given in Table A.1. This solution was used for experiments ACP-1 and ACP-2.

Table A.1 Simulated Uranium Solution

Element	Starting Material	Compound Mass (grams)	Element Concentration (μg/ml)	Analyzed Concentration (a) (μg/ml)
Uranium	$UO_2(NO_3) \bullet 6\ H_2O$	1.3094	621	567±20

(a) The analyzed concentration is given at the 95% confidence limit.

A 0.6 gram/liter (600 μg/ml) uranium/5 gram/liter (5000 μg/ml) lanthanum solution was prepared by initially dissolving 6.0050 grams of lanthanum oxide (La_2O_3) in 50 ml of 3.2M nitric acid. The volume and concentration were calculated to give a 1.0M nitric acid solution upon dissolution. Once the dissolution was complete, the solution was diluted to a 1 liter volume with 1.0M nitric acid. Lanthanum nitrate hexahydrate ($La(NO_3)_3 \bullet 6\ H_2O$), calcined to a constant mass at 900°C, was used as the starting material to prepare the La_2O_3. The $La(NO_3)_3 \bullet 6\ H_2O$ was obtained from Fisher Scientific (Lot No. 915064). Once the 5 gram/liter lanthanum solution was prepared, 1.3047 grams of UNH were dissolved directly in the lanthanum solution. The UNH was obtained from Mallinckrodt and assayed 100.6%. The concentrated nitric acid used to prepare the 3.2 and 1.0M solutions was obtained from E. M. Science and assayed 69-71% (15.7M). The prepared and analyzed concentrations for the solution are given in Table A.2. This solution was used for experiments ACP-3, ACP-4, and ACP-5.

Table A.2 Simulated Uranium/Lanthanum Solution

Element	Starting Material	Compound Mass (grams)	Element Concentration (μg/ml)	Analyzed Concentration (a) (μg/ml)
Uranium	$UO_2(NO_3) \bullet 6\ H_2O$	1.3047	621	563±18
Lanthanum	La_2O_3	6.0050	5120	5117±75

(a) The analyzed concentrations are given at the 95% confidence limit.

Simulated Am/Cm Pretreatment Experiments

The simulated Tank 17.1 solution was prepared by dissolving the starting materials listed in Table A.3 in 2 liters of 1.0M nitric acid. This procedure simulates the tank contents following formic acid denitration. The exception to this practice was the dissolution of 1.4583 grams of manganese sulfate monohydrate ($MnSO_4 \bullet H_20$) in 8 ml of 3.2M nitric acid. The volume and concentration were calculated to give a 1.0M nitric acid solution upon dissolution. The concentrated nitric acid used to prepare the 3.2 and 1.0M solutions was obtained from E. M. Science and Fisher Scientific and assayed 69-71 and 69.6% (15.7M), respectively.

Table A.3 Starting Materials for Simulated Tank 17.1 Solution

Element	Starting Material	Manufacturer	Lot No.	Assay
Lanthanum	$La(NO_3)_3 \bullet 6\ H_2O$	Fisher Scientific	947511	Laboratory Grade
Cerium	$Ce(NO_3)_3 \bullet 6\ H_2O$	Aldrich Chemical Company	01108PY	99% (1-2% La)
Praseodymium	$Pr(NO_3)_3 \bullet 6\ H_2O$	Aldrich Chemical Company	12513AN	99.9%
Neodymium	$Nd(NO_3)_3 \bullet 6\ H_2O$	Aldrich Chemical Company	18618MF	99.9%
Samarium	$Sm(NO_3)_3 \bullet 6\ H_2O$	Johnson Matthey	B16F16	99.9%
Europium	$Eu(NO_3)_3$	Johnson Matthey	P1148	99.9%
Gadolinium	$Gd(NO_3)_3 \bullet 6\ H_2O$	Aldrich Chemical Company	00630PF	99.9%
Aluminum	$Al(NO_3)_3 \bullet 9\ H_2O$	Fisher Scientific	942038C	98.80%
Calcium	$Ca(NO_3)_2 \bullet 4\ H_2O$	E. M. Science	33141329	99.00%
Iron	$Fe(NO_3)_3 \bullet 9\ H_2O$	J. T. Baker	C13332	99.6%
Potassium	KNO_3	Mallinckrodt	45059	>99%
Manganese	$MnSO_4 \bullet H_2O$	E. M. Science	34187506	99.0 - 101.0%
Sodium	$NaNO_3$	Fisher Scientific	941644B	100.10%
Nickel	$Ni(NO_3)_2 \bullet 6\ H_2O$	J. T. Baker	45059	99.60%

The prepared and analyzed concentrations for the simulated solution are given in Table A.4. This solution was used for experiments ACP-6, ACP-7, ACP-8, ACP-9, and ACP-10.

Table A.4 Element Concentrations in Simulated Tank 17.1 Solution

Element	Compound Mass (grams)	Element Concentration (µg/ml)	Analyzed Concentration (a) (µg/ml)
Lanthanum	4.3667	700	712±6
Cerium	4.9993	807	775±14
Praseodymium	4.9513	802	797±6
Neodymium	10.3331	1700	1674±12
Samarium	2.9700	502	522±5
Europium	2.2237	500	374±3
Gadolinium	1.8452	321	312±2
Aluminum	29.7931	1071	1002±11
Calcium	0.7778	66	65±1
Iron	71.6829	4955	5322±87
Potassium	1.1123	215	205±2
Manganese	1.4583	237	224±3
Sodium	4.9724	673	682±6
Nickel	2.2714	229	215±3

(a) The analyzed concentrations are given at the 95% confidence limit.

Slurry Properties of Oxalate Precipitate

Simulated solutions used to measure the slurry properties of the oxalate precipitate were prepared by dissolving the nitrate (and sulfate) salts of the lanthanide and metal impurities in a measured volume of 1.0M nitric acid. The concentrated nitric acid used to prepare the solutions was obtained from Fisher Scientific and assayed 69.6% (15.7M). The starting materials used to prepare the simulated solutions for experiments ACP-11, ACP-12 and ACP-13 were the same as listed in Table A.3. The materials used for experiment ACP-14 were also the same except for those listed in Table A.5.

Table A.5 Starting Materials for Simulated Tank 17.1 Solution for Experiment ACP-14

Element	Starting Material	Manufacturer	Lot No.	Assay
Europium	$Eu(NO_3)_3 \bullet 5\ H_2O$	Aldrich Chemical Company	01323LF	99.9%
Iron	$Fe(NO_3)_3 \bullet 9\ H_2O$	Mallinckrodt	5032KPPR	98.2%

The prepared and analyzed concentrations for experiments ACP-11, ACP-12, ACP-13, and ACP-14 are given in Tables A.6 - A.9, respectively.

Table A.6 Element Concentrations in Simulated Tank 17.1 Solution for Experiment ACP-11
Volume 0.250 liters

Element	Compound Mass (grams)	Element Concentration (μg/ml)	Analyzed Concentration (a) (μg/ml)
Lanthanum	3.1372	4026	4157±72
Cerium	3.6879	4760	4757±134
Praseodymium	3.5500	4600	4605±50
Neodymium	7.4723	9835	9762±92
Samarium	2.1294	2881	2996±31
Europium	1.6194	2912	2206±19
Gadolinium	1.3023	1815	1792±20
Aluminum	21.4553	6173	5930±121
Calcium	0.5559	377	379±12
Iron	51.6865	28580	30409±382
Potassium	0.8102	1253	1186±15
Manganese	1.0400	1352	1330±38
Sodium	3.5779	3871	3961±50
Nickel	1.6146	1303	1256±28

(a) The analyzed concentrations are given at the 95% confidence limit.

Table A.7 Element Concentrations in Simulated Tank 17.1 Solution for Experiment ACP-12
Volume 0.250 liters

Element	Compound Mass (grams)	Element Concentration (µg/ml)	Analyzed Concentration (a) (µg/ml)
Lanthanum	4.7733	6125	6199±59
Cerium	5.3552	6912	6893±67
Praseodymium	5.3275	6903	6750±81
Neodymium	11.1350	14656	14217±146
Samarium	3.2792	4437	4512±50
Europium	2.4322	4374	3235±35
Gadolinium	1.9780	2756	2649±31
Aluminum	32.3767	9315	8804±152
Calcium	0.8394	570	581±29
Iron	77.3794	42786	44204±1615
Potassium	1.3233	2047	1923±83
Manganese	1.5748	2048	1980±27
Sodium	5.3613	5801	5894±64
Nickel	2.4468	1975	1868±8

(a) The analyzed concentrations are given at the 95% confidence limit.

Table A.8 Element Concentrations in Simulated Tank 17.1 Solution for Experiment ACP-13
Volume 0.250 liters

Element	Compound Mass (grams)	Element Concentration (µg/ml)	Analyzed Concentration (a) (µg/ml)
Lanthanum	4.7182	6054	6406±99
Cerium	5.4147	6989	7130±125
Praseodymium	5.3441	6924	7159±121
Neodymium	11.1457	14670	14735±220
Samarium	3.2261	4365	4719±85
Europium	2.2517	4050	3120±49
Gadolinium	1.9630	2736	2753±45
Aluminum	3.7115	1068	991±28
Calcium	0.0965	66	(b)
Iron	8.9603	4955	5386±257
Potassium	0.1377	213	207±18
Manganese	0.1857	241	236±5
Sodium	0.6198	671	711±12
Nickel	0.2848	230	231±4

(a) The analyzed concentrations are given at the 95% confidence limit.
(b) Analytical results were not available.

Table A.9 Element Concentrations in Simulated Tank 17.1 Solution for Experiment ACP-14
Volume 2.000 liters

Element	Compound Mass (grams)	Element Concentration (µg/ml)	Analyzed Concentration (a) (µg/ml)
Lanthanum	37.7481	6055	6536±109
Cerium	42.8215	6909	7248±245
Praseodymium	42.6625	6910	7342±79
Neodymium	89.2600	14686	15146±135
Samarium	25.6482	4338	4859±72
Europium	24.3251	4318	4377±123
Gadolinium	15.6899	2733	2791±55
Aluminum	29.7593	1070	1034±37
Calcium	0.7751	66	(b)
Iron	71.6125	4950	5117±240
Potassium	1.1187	216	198±5
Manganese	1.4596	237	239±8
Sodium	4.9628	671	715±35
Nickel	2.2547	228	232±9

(a) The analyzed concentrations are given at the 95% confidence limit.
(b) Analytical results were not available.

Appendix B - Preparation of Oxalic Acid Solutions

The 0.9M oxalic acid solutions used for the precipitations were prepared by dissolving a measured mass of oxalic acid dihydrate ($H_2C_2O_4 \bullet 2\ H_2O$) in deionized water and diluting to a measured volume with deionized water. A summary of the solution preparation for each experiment is presented in Table B.1.

Table B.1 Preparation of Oxalic Acid Solutions

Exp't	Manufacturer	Lot No.	Assay (%)	$H_2C_2O_4 \bullet 2\ H_2O$ Mass (grams)	Solution Volume (liters)	Conc'n (moles/liter)
ACP-1 ACP-2 ACP-3	E. M. Science	32139330	99.5-102.5	113.4594	1.000	0.900
ACP-4 ACP-5	E. M. Science	30268417	99.5-102.5	113.4658	1.000	0.900
ACP-6 ACP-7 ACP-8 ACP-9 ACP-10 ACP-12 ACP-13	E. M. Science	30268417	99.5-102.5	226.9193	2.000	0.900
ACP-14	E. M. Science	30268417	99.5-102.5	226.9171	2.000	0.900
	E. M. Science	30268417	99.5-102.5	226.9610	2.000	0.900

The oxalate precipitation completed during experiment ACP-11 was mistakenly performed using a 0.25M oxalic acid/0.5M nitric acid solution originally prepared as a precipitate wash solution (see Appendix C). Approximately 17.9 grams of $H_2C_2O_4 \bullet 2\ H_2O$ were added to the graduated cylinder once the mistake was discovered to increase the excess oxalic acid concentration to 0.3M. This addition assumed complete precipitation of the lanthanides and complete solubility of the metal impurities.

Appendix C - Preparation of Oxalic Acid/Nitric Acid Wash Solutions

The 0.25M oxalic acid/0.5M nitric acid wash solutions were prepared by dissolving a measured mass of oxalic acid dihydrate ($H_2C_2O_4 \bullet 2\ H_2O$) in 0.5M nitric acid and diluting to a 2 liter volume with 0.5M nitric acid. The concentrated nitric acid used to prepare the 0.5M solutions was obtained from Fisher Scientific and assayed 69.6% (15.7M). A summary of the solution preparation for each experiment is presented in Table C.1.

Table C.1 Preparation of Oxalic Acid/Nitric Acid Wash Solutions

Exp't	Manufacturer	Lot No.	Assay (%)	$H_2C_2O_4 \bullet 2\ H_2O$ Mass (grams)	Solution Volume (liters)	$H_2C_2O_4$ Conc'n (moles/liter)
ACP-6 ACP-7	E. M. Science	30268417	99.5-102.5	63.0352	2.000	0.250
ACP-7	E. M. Science	30268417	99.5-102.5	63.0395	2.000	0.250
ACP-8	E. M. Science	30268436	99.5-102.5			
ACP-8 ACP-10 ACP-11	E. M. Science	30268436	99.5-102.5	63.0353	2.000	0.250

The oxalate precipitate generated during experiment ACP-9 was not washed due to problems with the stirrer operation.