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Mark-18A Ion Exchange Raffinate Management Strategy & Processing Recommendations

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EXECUTIVE SUMMARY

It is desired to recover Cm-244 through Cm-248 from dissolved Mark-18A targets following anion exchange processing to remove the Pu. The Cm will be sent to Oak Ridge National Laboratory (ORNL) for additional R&D. Approximately 5-8 L per quarter of a Mark-18A target will have undergone anion exchange treatment and will contain Cm. A significant portion of this volume of anion exchange raffinate solution is dissolved fission products not desired to be recovered which could be sent to waste. To reduce the amount of material being sent to ORNL, a waste and volume minimization strategy was developed and is described in this report.

Research presented in this report indicates that evaporation of the anion exchange raffinate to reduce the volume, followed by denitration through formic acid addition, produces a solution from which rare earth and transuranic metals can be precipitated by an oxalic acid strike. The metal oxalate precipitate solids are easily filterable and the filter cake can be calcined to convert the material to metal oxides, which are traditionally chemically stable.

During evaporation, water and nitric acid rich streams can be removed to significantly reduce the volume of the feed solution treated for denitration. These evaporator cut streams can likely be recycled within the flowsheet. Some Cs, 0.006 mg/L (2nd condensate cut from 1.5 L-scale test collected during continuous operations), was observed in the water rich cut. A higher amount of Cs (0.41 mg/L), along with Sr (0.11 mg/L) and some Sm (0.14 mg/L) were observed in the nitric acid-rich cut, though the Sm result is considered suspect.

Formic acid treatment was required to reduce the nitrate concentration to $< 1 \text{ M NO}_3^-$ to selectively precipitate rare earths and transuranic constituents. The study indicated that 0.88 moles of formic acid per mole of nitric acid was the minimum ratio needed to sufficiently destroy the nitrate anion. The residual nitric acid concentration had a greater impact on the selective precipitation of the rare earth metals tested (La, Ce, Pr, Nd, Sm, Eu, and Gd) than the residual formic acid concentration. As the ratio of the moles of formic to nitric acid was increased much above 1.0 the amount of residual formate ion increased, without a significant decrease in nitrate ion concentration. A target formic to nitric acid ratio between 0.90 and 1.06 is recommended. During formic acid treatment, a significant amount of NO_x gas is generated from the reduction of nitric acid. Analysis of the off gas produced did not detect hydrogen or ammonia. Formic acid addition causes foaming; therefore, it is necessary to control the reagent addition speed. During the 1.5 L scale experiment, the maximum formic acid rate was 2.3 ml/min. Formic acid treatment is the rate limiting step of the unit operations proposed.

Oxalic acid should be added in a stoichiometric excess of approximately 0.2 M or greater to promote selective precipitation of the rare earth elements studied. As the nitrate ion concentration increased, the decontamination factors (DFs) decreased significantly. The difficulty of precipitation appears to follow the order $\text{Eu} < \text{Sm} < \text{Gd} < \text{Nd} < \text{Pr} < \text{Ru} < \text{Ce} < \text{La}$. The Eu DF was ~ 1400 , whereas the La DF was ~ 6 . Cm is expected to behave like Sm, which had a DF of ~ 290 . Increasing the oxalic acid addition rate visually appears to produce smaller particles.

The oxalate precipitate slurry was able to flow through the 0.45 μm filter disk with little to no holdup in the filter housing and efficient separation of the oxalate precipitate was achieved. Filtration was performed with polycarbonate or polypropylene filters. With time, additional solids formed in the filtrate. A second filtration of the solution indicated that the solids are likely aluminum and sodium oxalate salts. Therefore, it is recommended to not delay filtering.

TGA-MS results indicate that the calcined product is dry, but a mass loss of ~ 1.6 wt% was observed that is likely due to volatilization of metal oxides rather than water. The volatilization of Cs or Na could be the source of the mass loss. Additional R&D is needed to confirm whether increased calcination time or calcination under forced air conditions would be sufficient to meet the less than 0.5 wt% loss on ignition programmatic target for packaging.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CN	Cellulose Nitrate
Cont.	Continuous Operations
DF	Decontamination Factor
HAD	High Activity Drain
IC-Anions	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IX	Ion Exchange
MCNP	Monte Carlo N-Particle Transport Code
ORNL	Oak Ridge National Laboratory
PC	Polycarbonate
PP	Polypropylene
PSAL	Process Support Analytical Laboratory
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TGA	Thermal Gravimetric Analysis

1.0 Introduction

Eighty-six Mark-18A targets were irradiated at the Savannah River Site (SRS) during the late 1960's to the late 1970's to produce specific heavy isotopes. Twenty one of these targets were processed at Oak Ridge National Laboratory (ORNL) to recover Pu-244, Cm-244 through Cm-248, and Cf-252 in the early 1970's. Sixty-five targets remain at SRS, stored in the L Spent Fuel Storage Basin. It has been proposed that the remaining targets be dissolved at the Savannah River National Laboratory (SRNL) to allow recovery and preservation of Pu-244, rare earth metals, and transuranic metals. SRNL has been tasked to develop a flowsheet to process the Mark-18A targets individually within the E-wing shielded cells facility.

It was necessary to adapt the ORNL flowsheet, previously used to process Mark-18A targets, to successfully process the materials within SRNL and identify process improvements. The Mark-18A target materials will be removed from their current packaging, dissolved, chemically separated, and calcined as outlined in Figure 1-1.

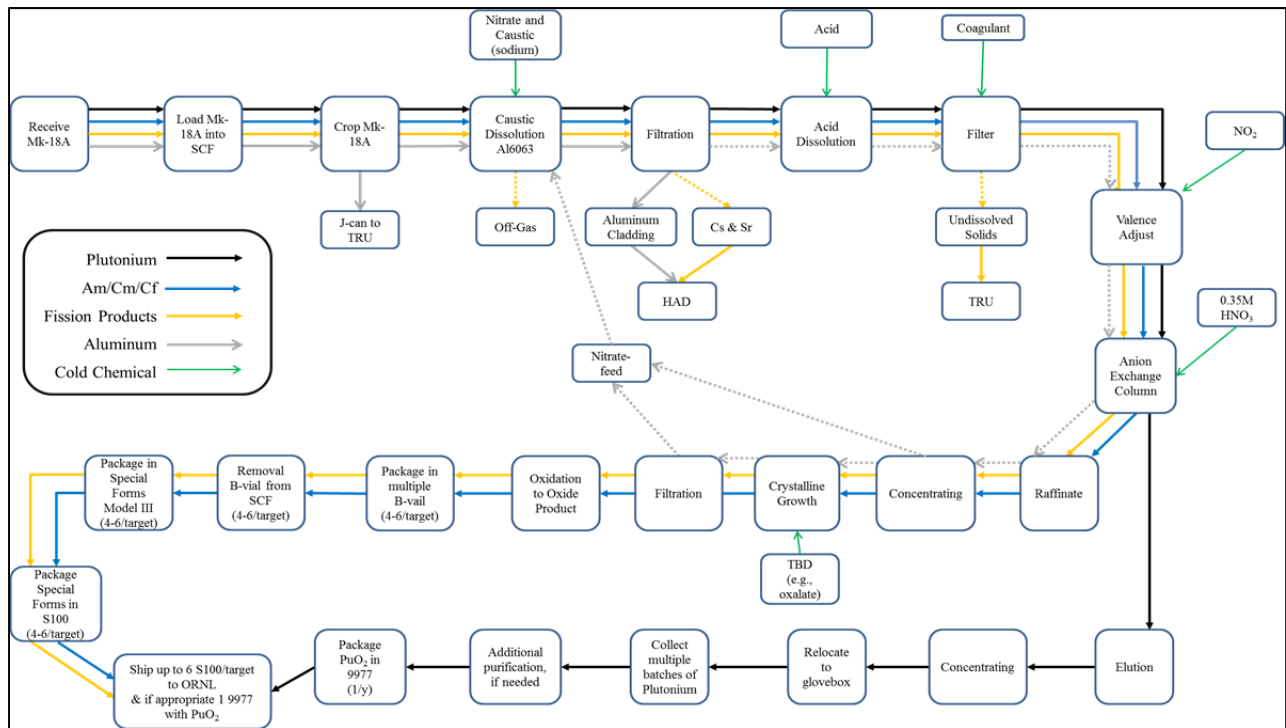


Figure 1-1. Mark-18A Target Processing Flowsheet Conceptual Design

The research presented in this paper is applicable to the chemical processing of the raffinate stream from the anion exchange column, as designated by the scope of work [1]. The final product form is expected to be a rare earth and transuranic metal oxide powder, which will be shipped to ORNL. The oxide will be packed in a Los Alamos Special Forms Capsule Model III container and shipped using a Department of Transportation approved Type A package. The treatment process and oxide product is expected to meet the following programmatic goals:

1. The material must be unreactive
2. The material must have a water content less than 0.5 wt%
3. Residual waste must be compatible with existing SRNL waste programs

2.0 Background

The expected chemical composition of the Mark-18A target was modeled using process knowledge, SCALE 6.1, and MCNP 6 [2]. The results were used to develop a non-radioactive simulant of the dissolved target for testing, described in Table 2-1 [3]. Sm was added to simulate Cm, excess Sr to simulate Ba, Nd to simulate Am, Re to simulate Tc, and excess Zn to simulate Cd. The simulant was then processed through an anion exchange column containing Reillex™ HPQ resin prior to being used for testing [4]. Reillex™ resin is well known to have a high affinity for Pu; however, experiments were performed to evaluate the distribution coefficients of the other major components in the Mark-18A material. The anion exchange testing is described in a separate report [4]. Two anion exchange raffinate, IX1 and IX2, became the feed solutions for the tests described in this report.

Table 2-1. Mark-18A Target and Simulant Composition¹

<u>Element</u>	<u>Mark-18A Target with Cladding, wt%</u>	<u>Uncladded Mark-18A Target, wt%</u>	<u>IX Column Simulant, wt%</u>	<u>IX1 Simulant Raffinate, wt%</u>	<u>IX2 Simulant Raffinate, wt%</u>
Al	95.88%	-	39.72% ²	38.62%	37.97%
Mg	0.67%	-	10.14% ²	10.36%	10.38%
Fe	0.29%	-	8.79% ²	9.03%	9.14%
Na	-	-	1.50% ²	1.59%	1.59%
Xe	0.36%	11.32%	-	-	-
Pu	0.32%	10.15%	-	-	-
Nd	0.29%	9.31%	5.90%	5.98%	5.99%
Ru	0.22%	6.93%	0.00% ³	0.00%	0.00%
Cd	0.18%	5.70%	See Zn	See Zn	See Zn
Zn	0.00%	0.00%	5.37%	5.15%	5.28%
Pd	0.32%	10.26%	0.43%	0.11%	0.29%
Ce	0.17%	5.47%	5.29%	5.37%	5.45%
Mo	0.14%	4.39%	0.79%	0.83%	0.80%
Gd	0.11%	3.40%	3.19%	3.28%	3.35%
Zr	0.09%	2.88%	0.20%	0.20%	0.21%
Cs	0.07%	2.29%	2.05%	2.09%	2.14%
La	0.06%	1.91%	1.72%	1.77%	1.77%
Pr	0.05%	1.50%	11.89%	12.16%	12.19%
Cm	0.37%	11.76%	See Sm	See Sm	See Sm
Sm	0.04%	1.37%	1.16%	1.18%	1.20%
Am	0.04%	1.19%	See Nd	See Nd	See Nd
Eu	0.01%	0.17%	0.80%	0.82%	0.83%
Te	0.04%	1.16%	-	-	-
Tc	0.02%	0.51%	See Re	See Re	See Re
Re	-	-	0.392%	0.40%	0.40%
Sn	0.01%	0.37%	0.00%	0.00%	0.00%
Sr	0.01%	0.28%	1.03%	1.06%	1.04%
Ba	0.17%	5.48%	See Sr	See Sr	See Sr

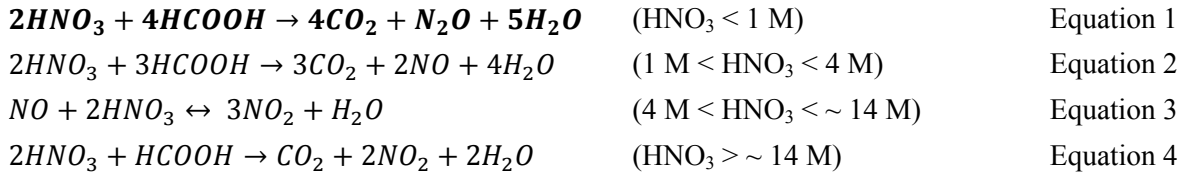
Given the number of undesirable dissolved materials expected to be present in the IX raffinate, methods were developed to separate the desired rare earth and transuranic metals from the bulk raffinate to reduce the amount of material shipped to ORNL. Literature indicates that separation of rare earth and transuranic metals is feasible using an oxalic acid strike, in excess of stoichiometric requirements, if the nitric acid concentration is sufficiently low [5, 6]. The rare earth and transuranic metal oxalate precipitate is typically filterable from the solution. Upon collection of the metal oxalate solids, the rare earth and transuranic metals would be converted to an oxide form via calcination.

¹ Some elements were substituted with similar behaving ones that were non-radioactive or more readily available [4].

² Added to emulate carryover after dissolution of the Mark-18A target.

³ Ru was added as 0.70 grams of RuO₂. Sn was added as 0.29 grams of SnO₂. However, it was stated that Ru and Sn did not appear to dissolve completely [4].

The ideal nitric acid concentration was reported to be < 1 M to produce the highest selective yield of rare earth and transuranic precipitate based on experiments performed by Rudisill [5, 6]. The anion exchange raffinate is expected to be 7-9 M HNO₃, thus it was necessary to develop a pretreatment step to reduce the nitric acid concentration. Formic acid has been frequently used to destroy nitrate anions successfully. The denitration proceeds according to the overall reactions given in Equation 1 through Equation 4 [7-10]. When nitric acid is decreased from > 14 M, and < 4 M, the reaction kinetics shift from Equation 4 to Equation 2, while Equation 3 applies at intermediate concentrations. More NO₂ is produced at > ~ 8 M HNO₃, and more NO is produced for HNO₃ concentrations < ~ 8M [7].



The anion exchange raffinate volume is expected to be approximately 5-8 liters per quarter of a dissolved Mark-18A target, thus a significant amount of formic acid would be required to denitrate the feed for oxalic acid precipitation. The subsequent addition of oxalic acid solution to promote precipitation further increases the amount of liquid waste requiring disposition to the high activity drain (HAD). Therefore, evaporation of excess material from the anion exchange raffinate was conducted to minimize the waste needing to be dispositioned, and consideration was given to recycling the distillate within the flowsheet.

As demonstrated in Figure 2-1, nitric acid systems have an azeotrope between 67% and 68% HNO₃ (14.9 M - 15.1 M). Thus, as the water in the anion exchange raffinate evaporates, causing the boiling point to rise, the concentration of nitric acid in the vapor form increases until the concentration in the vapor and liquid are equal (azeotropic boiling). This solution property can be used to remove two cuts of recycle during evaporation: a water rich cut and a nitric acid rich cut.

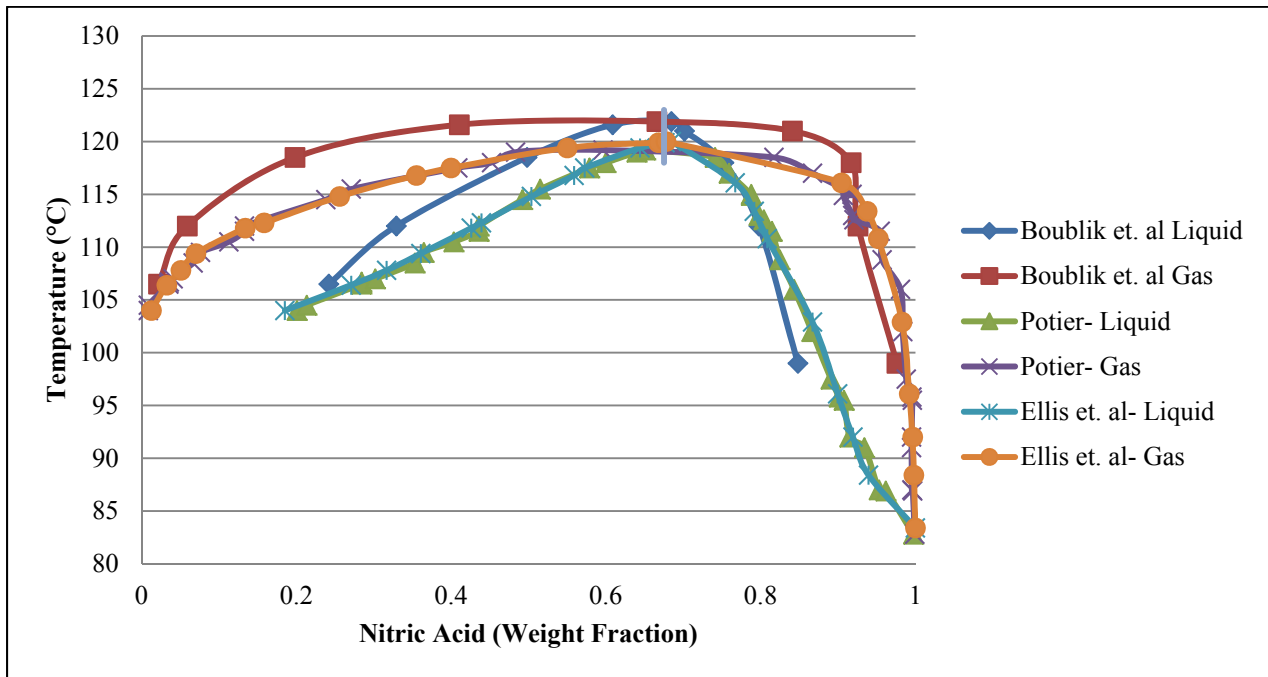


Figure 2-1. Nitric Acid Vapor Liquid Equilibrium Diagram

Removing the two cuts for recycle will reduce the amount of formic acid required for reaction and reduce the volume of material to be filtered after performing the oxalic acid strike to precipitate the rare earth and transuranic metals as oxalate solids.

3.0 Experimental Procedure

Non-radioactive anion exchange raffinate was supplied from the anion exchange testing described in a separate report [4]. This work focuses on concentration of the raffinate prior to denitration, oxalate precipitation, filtration, and calcination.

3.1 Concentration of Raffinate

Initial evaporation tests involved a fractionating column. Fractionating columns typically can be used to remove a more pure water rich cut by distillation prior to azeotropic boiling. The glass column was heated with a 430 W heating mantle. Results indicated that the equipment could not reach the necessary boilup rate to reduce the raffinate volume within a reasonable amount of time. Therefore, a single stage evaporation unit was also tested. Equipment can be seen in Figure 3-1. Neoprene and glass wool were used for insulation.

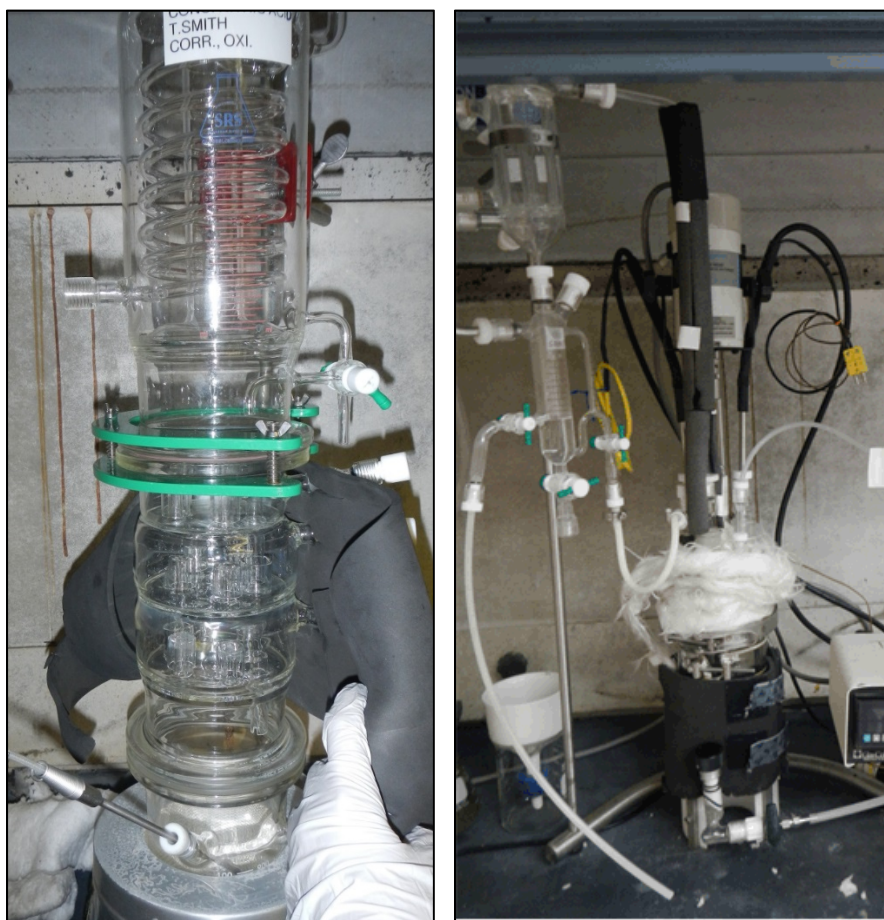


Figure 3-1. Fractionating Column (Left) and Single Stage Evaporation Unit (Right)

Two tests were performed in the fractionating column with 11 M nitric acid containing no metal additives to evaluate the equipment. The column contained three fractionating chambers. Two tests using the fractionating column were performed with the anion exchange raffinate simulant, while the new single stage evaporation equipment was setup. For all evaporation tests, a pre-weighed solution was added to the vessel. The solution was then heated to boiling. The condenser temperature was maintained at 13-15 °C during evaporation to collect condensate. The goal was to evaporate the solution to as low a volume as achievable within a reasonable and appropriate amount of time and then assess downstream impacts. The equipment design was evaluated against the following:

1. Boil-up rate of condensate
2. Carry-over of metals in condensate
3. Mass balance (volume reduction)
4. Ease of use

The boilup rate was determined with a stopwatch, while observing the graduated markings on the condensate reservoir. Samples from the condensate and concentrated raffinate were sent to the Process Support Analytical Laboratory (PSAL) or Analytical Development (AD) for ion chromatography (IC-anions) and inductively coupled plasma (ICP). ICP mass spectrometry (MS) and/or atomic emission spectroscopy (AES) were used to qualify the inorganic content of the samples. The condensate and the remaining, concentrated anion exchange raffinate were weighed upon completion of each test.

3.2 Denitration by Formic Acid Addition

Concentrated formic acid (88-90 wt%) was pumped into a pre-weighed 100 mL sample of the concentrated anion exchange raffinate in a 250 mL volumetric flask that was heated to 90 °C, while stirring at 200 – 300 rpm. The formic acid addition flow rate and the ratio of total formic acid to the initial nitric acid concentration were varied to evaluate the effects on nitrate destruction efficiency. Upon completion of formic acid addition, the system was held at 90 °C for two hours. The concentrated raffinate was sampled periodically to track the anion concentration over time. Samples were sent to PSAL or AD for IC-anion analysis. The final product was weighed to determine the mass loss resulting from NO_x off gassing. For some experiments, the product was also sampled to determine the metal content via ICP-MS and/or ICP-AES.

3.3 Oxalate Precipitation

Two types of studies were performed for oxalate precipitation. One study involved a simple simulant and the other involved the remaining concentrated raffinate previously processed for nitrate destruction. The simple simulant contained the major species in the anion exchange raffinate simulant and two rare earths of interest (see Table 3-1). The simulant was prepared from the metal nitrate salts. The simple simulant was used to better evaluate effects of various experimental processing parameters including temperature, oxalic acid addition rate, processing time, total quantity of oxalate added, and starting nitric/formic acid concentrations on the recovery of the rare earth materials, since the simulant provided a consistent starting point for comparison.

Table 3-1. Simple Simulant

<u>Component</u>	<u>Result</u>	
Free Acid	0.30	M
Total Acid	1.96	M
Nitrite	< 100	mg/L
Nitrate	168,000	mg/L
	2.71	M
Al	14700	mg/L
Fe	3200	mg/L
La	3670	mg/L
Mg	4330	mg/L
Na	3630	mg/L
Sm	1744 ⁴	mg/L

3.3.1 Simple Simulant Tests

Oxalic acid was added, in a range of 0.15 – 0.35 molar excess of the stoichiometric amount needed, to 90 mL of the simple simulant in a 250 mL volumetric flask. For two tests, 0.83 M oxalic acid was mixed with isopropyl alcohol (70 wt% isopropyl alcohol solution was used). Isopropyl alcohol was added to target a final concentration of 10 vol%. Aliphatic alcohols, when mixed with an oxalate containing solution have been found to significantly increase the precipitation yield of rare-earths [11]. The oxalate solution was pumped into the simulant, while it was between 50 – 80 °C and the mixture was stirred at 300 rpm. Upon completion of the oxalate addition, the system was allowed to digest for 2 – 4 hours, while stirring, and the temperature was lowered to 45°C. The matrix of experiments performed can be seen in Table 3-2.

⁴ Calculated based on the mass added.

Table 3-2. Simple Simulant Metal Oxalate Precipitation Matrix

<u>Test #</u>	<u>Temp, °C</u>	<u>Initial Nitrate Conc., M</u>	<u>Initial Formate Conc., M</u>	<u>Oxalic Acid Addition Speed, mL/min</u>	<u>Digestion Time, hr</u>	<u>Oxalic Acid Reagent Addition</u>	<u>Excess Oxalic Acid Stoichiometry, M</u>
1	60	0.3	1.3	2.61	2	0.83 M aqueous	0.30
2	60	0.3	1.3	2.61	2	0.83 M aqueous	0.30
3	60	0.3	1.3	2.61	2	0.83 M aqueous	0.35
4	60	0.3	1.3	2.61	2	0.83 M aqueous	0.35
5	60	0.3	1.3	3.48	2	0.83 M aqueous	0.25
6	60	0.3	1.3	3.48	2	0.83 M aqueous	0.25
7	60	0.3	1.3	2.61	4	0.83 M aqueous	0.15
8	60	0.3	1.3	2.61	4	0.83 M aqueous	0.15
9	60	0.3	1.3	Cont. ⁵	2	0.83 M aqueous	0.20
10	60	0.3	1.3	Cont. ⁵	2	0.83 M aqueous	0.27
11	60	1	1.3	2.61	2	0.83 M aqueous	0.30
12	60	1	1.3	2.61	2	0.83 M aqueous	0.30
13	80	0.3	1.3	2.61	2	0.83 M aqueous	0.30
14	80	0.3	1.3	2.61	2	0.83 M aqueous	0.30
15	50	0.3	1.3	2.61	2	0.83 M aqueous	0.30
16	50	0.3	1.3	2.61	2	0.83 M aqueous	0.30
17	60	0.3	1.3	2.61	2	0.83 M aqueous with isopropanol	0.35
18	60	0.3	1.3	2.61	2	0.83 M aqueous with isopropanol	0.35
19	60	0.3	2	2.61	2	0.83 M aqueous	0.30
20	60	0.3	2	2.61	2	0.83 M aqueous	0.30

⁵ For tests 9 and 10, the oxalic acid and simulant were both pumped in at 2.61 mL/min; this is denoted as continuous operations ('cont.').

3.3.2 Denitrated, Concentrated Anion exchange Raffinate

For precipitation studies with the anion exchange simulant, following evaporation and denitration, the simulant was heated to 60-70 °C, while stirring at 250-300 rpm, then 0.55-0.83 M oxalic acid was added by syringe pump at the appropriate rate. Upon completion of the addition, the temperature was dropped to 45 °C and held for 2 hours before it was filtered. A summary of the experimental parameters can be seen in Table 3-3.

Table 3-3. Denitrated, Concentrated Anion Exchange Raffinate Matrix

<u>Experiment ID</u>	<u>Starting Material</u>	<u>Temp., °C</u>	<u>Oxalate Conc. Added, M</u>	<u>Stir Speed, RPM</u>	<u>Aging Time, Hr</u>	<u>Oxalate Addition Speed, mL/min</u>
NF1-0.70	IX1	60	0.83	300	2	2.61
NF1-0.75	IX2	60	0.83	300	2	2.61
NF1-0.85	IX1	60	0.83	300	2	2.61
NF1-0.88	IX2	70	0.55	250	2	1.5
NF1-0.88B	IX2	70	0.55	250	2	1.5
NF1-0.90	IX1	60	0.83	300	2	2.61
NF1-0.90B	IX2	60	0.83	300	2	1.3
NF1-1.05	IX1	70	0.55	250	2	1.5

3.4 Filtration

Prior to performing filtration tests with the precipitated simple simulant and denitrated, concentrated anion exchange raffinate, various filter paper types were evaluated as shown in Table 3-4. The filters were calcined to determine residual ash content. Those with negligible ash content were submerged in 3.9 M nitric acid for two weeks to evaluate chemical durability.

Table 3-4. Disk Filters Evaluated for Use in Metal Oxalate Filtration

<u>Filter Type</u>	<u>Manufacturer</u>	<u>Size</u>	<u>Model</u>	<u>Lot#</u>
Cellulose Nitrate (CN)	MFS Disk	90 mm disk, 0.1 µm	A010A090C	Lot # 82067
Polypropylene (PP)	Pall Life Science	47 mm Disk, 0.45 µm	56548	Lot # T00732
Polycarbonate (PC)	Costar	47 mm disk, 0.4 µm	3962	Lot # 3962
Polycarbonate (PC)	Whatman Nucleopore	47 mm disk, 0.4 µm	111107	Lot # 1087001

The precipitates prepared from both the simple simulant and the denitrated, concentrated anion exchange raffinate were filtered using 47 mm filter disks. The filter disks were held in place in a magnetic filter unit with a platform. The platform allowed the slurry solids to collect in the magnetic housing. The filter housing was inserted into a 1 L filtrate collection flask that contained a pre-weighed, 60 mL centrifuge tube. Centrifuge tubes were used to collect the filtrate because their convenient geometry allows ease of

filtrate collection. The filtrate collection flask was connected to the lab house vacuum via flexible polymer tubing. Each oxalate precipitate slurry was added to the top of the filter unit either by pouring or using a transfer pipet. Centrifuge tubes were changed out as needed to collect all of the filtrate. Upon filtering all of the slurry for a given test, a wash solution was added to the now empty volumetric precipitate flask. The wash solution was then pipetted over the wet filter cake to serve as a rinse. The wash solution contained 0.5 M nitric acid and 0.25 M oxalic acid. All wash filtrate was collected in a separate centrifuge tube. The filtrate was weighed, sampled and sent to AD for ICP-MS, free acid, total acid, ICP-AES and/or IC-anion analysis to determine the effectiveness of the oxalic acid precipitation.

The wet cake and filter paper were placed on a watch glass and allowed to dry under ambient conditions for a minimum of 12 hours.

3.5 Calcination

The air dried solid cake and filter paper were placed into a pre-weighed 50-mL glazed alumina crucible. The crucible was then reweighed and placed into the furnace. The furnace was programmed to heat at 8 °C/min up to 200 °C, hold for 50 min to drive off the water, then the temperature was increased at the same rate to 1000 °C and held for 2 hours. The material was allowed to cool in the furnace to a temperature near 100 °C. It was then removed, and placed in a desiccator overnight to cool. The crucible containing the oxide was weighed to determine the final product weight. Some of the calcined material was sent for total gravimetric analysis (TGA), total gravimetric analysis mass spectrometry (TGA-MS), and carbon/sulfur, as well as ICP-MS and/or ICP-AES after peroxide fusion.

3.6 Scaling Experiment

The 1-L single stage evaporator was operated at ambient pressure in a semi-continuous mode to process a total feed of 1.5-L. Due to the work shift schedule, the experiment was stopped after each unit operation and allowed to sit without heating or agitation overnight.

The IX2 feed, described in Table 2-1, was used for the 1.5-L experiment. All chemical and simulant additions were introduced below the liquid surface. For all unit operations the mixer speed was set to 300 rpm and the condenser was operated at 15 °C. One liter of pre-weighed simulant was added to the vessel. During evaporation, the system was heated to boiling. The boilup rate was determined using a stop watch and the graduated markings on the condensate collection reservoir. To prevent overflowing, ~350 grams (~345 mL) of condensate was removed from the system before the simulant addition pump was started. The simulant addition rate was adjusted to not exceed volume losses from boiling. The boilup rate was monitored to evaluate any changes as a result of continuous operations. It was targeted to remove ~ 1.2 L of condensate from the system as two cuts: a water rich and a nitrate rich. Condensate was drained from the condensate collection reservoir into plastic bottles. Based on the known simulant anion concentrations and the vapor liquid equilibrium diagram (Figure 2-1), the water rich cut volume should be approximately 850 mL and the nitric acid rich cut would be ~ 350 mL.

After evaporating the desired volume, the water rich condensate, nitric acid rich condensate, and concentrated anion exchange raffinate were sampled. Samples were analyzed by AD for ICP-MS, ICP-AES, free acid, density, and IC-anions. The experiment was stopped overnight. The next day a small amount of additional condensate was observed in the condensate collection reservoir, which was drained and sampled. The next day it was determined that too much liquid volume had been removed from the system because the solution did not fully cover the heated area of the heating rods when stirred. Thus ~190 mL of DI water was added to the vessel. The heating rod current was then adjusted to target a vessel temperature of 90 °C.

Formic acid (88 wt%) was then added subsurface at a total molar ratio of 1.06 moles of formic acid to nitric acid by FMI pump at a rate of 2.31 mL/min. During the formic acid addition step, the off gas exiting the condenser was sampled periodically in 1 L Tedlar[®] bags. The bagged samples were exhausted through a RAMAN spectrometer to check for hydrogen and ammonia. After completing the formic acid addition, the material was allowed to process for two hours before being sampled. A small amount of condensate (~80 mL) was collected during denitration. This condensate was drained into plastic bottles and then sampled. The denitrated, concentrated anion exchange raffinate and the condensate were sent to AD for ICP-MS, ICP-AES, IC-anions, density, and free acid. The experiment was then stopped at the end of the day.

The following morning, the heating rod controller was adjusted to target a vessel temperature of 60 °C, while stirring. Oxalic acid (0.83 M) was pumped by FMI pump subsurface into the vessel at a rate of 8.0 mL/min. Oxalic acid was added to target a 0.1 M excess of the stoichiometric amount required, which was 0.1 M (resulted in an addition of 0.2 M). The temperature was then lowered to 45 °C and the material was allowed to digest for two hours. The temperature was lowered to 35 °C to simulate the resting system temperature of the radiolytic mixture. While stirring, the material was drained from the bottom of the vessel through a 5" cellulose nitrate filter disk placed in a glazed alumina filter casing. The filtrate was sampled and sent to AD for ICP-MS, ICP-AES, IC-anions, free acid, and density. No wash was performed. The precipitate was allowed to dry overnight on a watch glass before being calcined. The filter disk containing the wet filter cake was calcined in an alumina crucible. The furnace was programmed to heat at a rate of 8 °C/min up to 200 °C, hold for 50 min to drive off the water, then ramped up at the same rate to 1000 °C and hold for 2 hours. After cooling in a desiccator, the product solids were sent for TGA-MS analysis and carbon/sulfur. ICP-MS and ICP-AES analyses were also conducted following solids digestion/dissolution by peroxide fusion.

3.7 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

4.0 Results and Discussion

4.1 Concentration of Raffinate Results

Two nitric acid only test runs (N1 and N2) were performed with the fractional distillation column setup (see Figure 3-1) to evaluate the equipment. Operating conditions (times, temperatures, and volumes) recorded during testing are provided in Figure 4-1. The glass vessel cracked due to thermal shock during the second test, thus a rheostat was used to adjust the heating voltage and the test was repeated. During, run N2 the rheostat was set to 8. The evaporator pot temperature increased at a rate of ~5°C/min (Figure 4-1), which is equivalent to ~ 460 KJ/(kg min) or a 0.1% efficiency. The condenser was operated at 13-15 °C. Once boiling was achieved (~122 °C) the average boilup rate of the system was 1.7 mL/min.

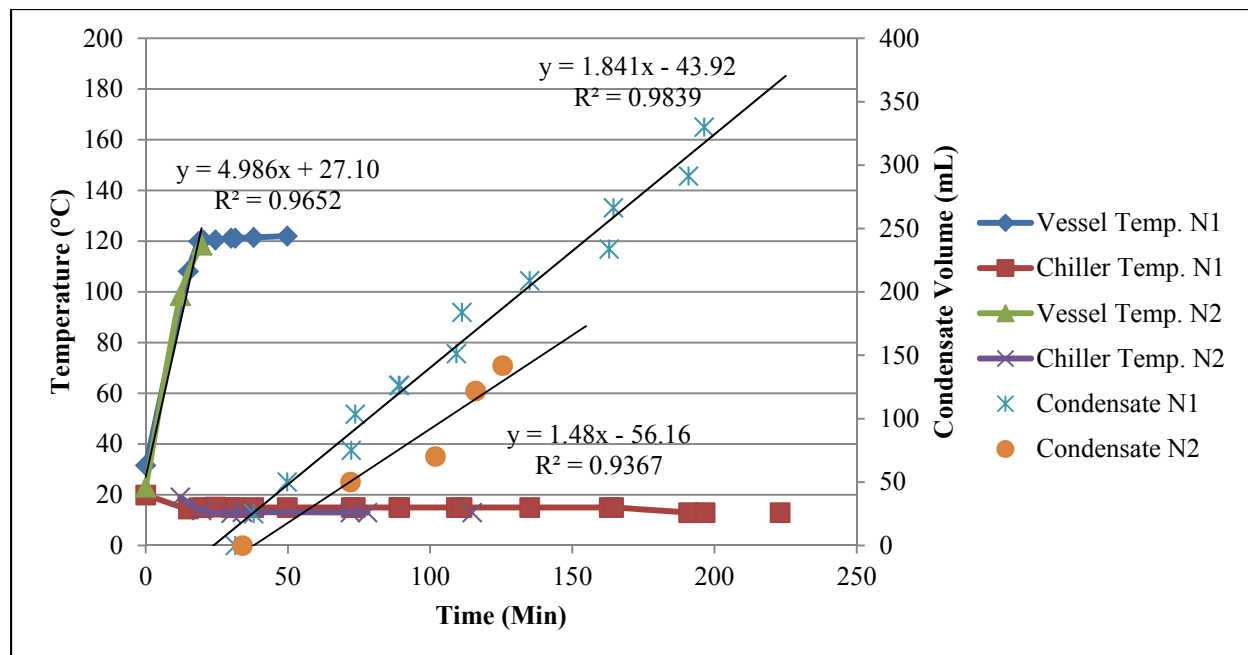


Figure 4-1. Fractional Distillation Column Conditions during Nitric Acid Only Testing⁶

The low efficiency of the system would require 10 hours to collect 1 liter of condensate; therefore, a new system was developed. It was decided to continue testing with the fractional distillation column while the new system was being designed and built. Two fractional distillation runs were performed with anion exchange simulants (IX1 and IX2). Operating conditions (times, temperatures, and volumes) recorded during testing are provided in Figure 4-2. During IX1 testing, boiling was observed at ~111 °C. To determine the experimental time IX2 started boiling, the initial heating profile was extrapolated as seen by the red dashed line in Figure 4-2. During IX2 testing, boiling initiated around 54 minutes. The average boilup rate of the anion exchange simulants was 1.5 mL/min. During boiling, NO_x gases were visually observed in the vapor space.

⁶ Data displayed in Appendix A.

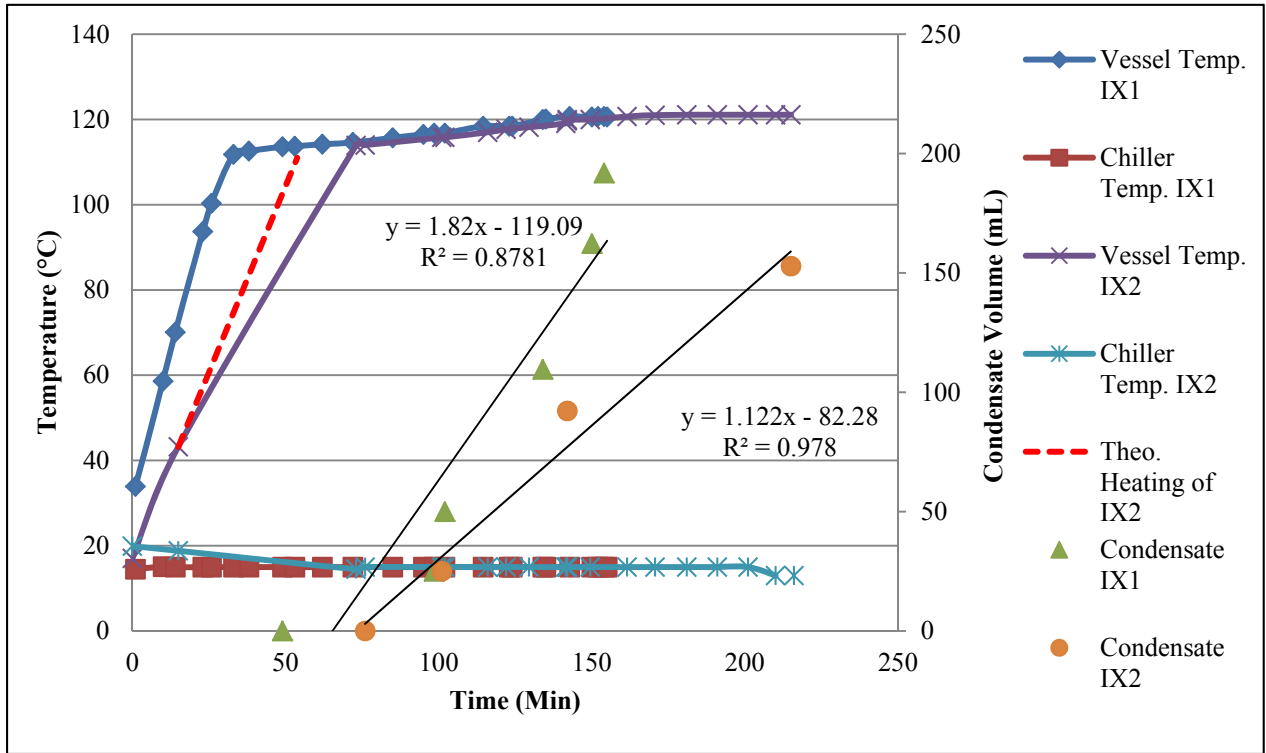


Figure 4-2. Fractional Distillation of Anion exchange Simulant⁶

Carryover of the anion exchange simulant, as a result of entrainment, was evaluated by sampling the bottom, middle, and top bubble trays in addition to the condensate collection tank at various process times. The results, seen in Table 4-1, indicate some entrainment carryover of material through the top tray during IX1 run and through the middle tray during the IX2 run. Ce, Eu, Gd, La, Mo, Nd, Pb, Pr, Re, Ru, Sr, Sm, Sn, Sr, Zn, and Zr were all less than detectable (< 1.00 mg/L). Cs was unable to be analyzed due to an analytical equipment outage. Minimal metal concentrations were expected in the trays because of the low expected entrainment of the metal salts.

Table 4-1. Metal Entrainment Carryover Evaluation for the Fractional Distillation Apparatus

<u>Location</u>	<u>Time Corrected to Start of Boiling, min</u>	<u>Sample ID</u>	<u>Al, mg/L</u>	<u>Fe, mg/L</u>	<u>Mg, mg/L</u>	<u>Na, mg/L</u>	<u>Fe/Mg Ratio</u>	<u>Fe/Na Ratio</u>	<u>Mg/Na Ratio</u>
IX1 Feed	Initial	N/A	3535	900	1028	161	0.875	5.59	6.39
IX2 Feed	Initial	N/A	3718	943	1079	167	0.874	5.65	6.46
Bottom Tray	90.00	IX1-4	<1.00	7.29	3.64	1.42	2.004	5.124	2.556
Bottom Tray	117.00	IX1-8	<1.00	6.61	3.25	1.29	2.032	5.138	2.528
Bottom Tray	68.18	IX2-2	<1.00	1.23	<1.00	<1.00	N/A	N/A	N/A
Bottom Tray	107.68	IX2-6	<1.00	<1.00	<1.00	<1.00	N/A	N/A	N/A
Middle Tray	90.00	IX1-3	1.09	14.09	8.22	1.76	1.714	8.000	4.668
Middle Tray	117.00	IX1-7	<1.00	11.25	6.49	1.36	1.733	8.279	4.777
Middle Tray	68.18	IX2-3	<1.00	1.85	<1.00	<1.00	N/A	N/A	N/A
Middle Tray	107.68	IX2-7	<1.00	1.19	<1.00	<1.00	N/A	N/A	N/A
Top Tray	90.00	IX1-2	<1.00	8.49	4.74	1.29	1.794	6.578	3.668
Top Tray	117.00	IX1-6	<1.00	4.53	2.14	<1.00	N/A	N/A	N/A
Top Tray	68.18	IX2-4	<1.00	<1.00	<1.00	<1.00	N/A	N/A	N/A
Top Tray	107.68	IX2-8	<1.00	<1.00	<1.00	<1.00	N/A	N/A	N/A
Top Condensate	121.00	IX1-10	<1.00	<1.00	<1.00	1.03	N/A	N/A	N/A
Top Condensate	161.18	IX2-10	<1.00	<1.00	<1.00	<1.00	N/A	N/A	N/A

As seen in Table 4-2, it appears that with additional time at boiling fewer metals were transferred to the trays, which may be a result of reaching a steady state. In comparing the relative ratios, the Mg carryover appears lower relative to Na and Fe carryover in the bottom and top bubble tray. The middle tray may have low sodium and possibly increased iron. Al results are low compared to Mg and Fe, which may indicate that Al is precipitating. The middle tray receives material from both the bottom and top trays. It is clear that carryover is not uniform. Interestingly, the relative ratios within each tray appear to stay constant over time. Additional data points would be needed to confirm if carryover is actually occurring. The percent carryover based on the material loaded into the vessel was determined, as seen in Table 4-2. Results that were less than detection were assumed to be at the detection limit for conservatism.

Table 4-2. Percent Carryover during Fractional Distillation with IX1 and IX2 Raffinates

<u>Experiment</u>	<u>Time Corrected to Boiling</u>	<u>Sample Location</u>	<u>Al</u>	<u>Fe</u>	<u>Mg</u>	<u>Na</u>
IX1	90	bottom tray	0.03%	0.81%	0.35%	0.88%
	90	middle	0.03%	1.57%	0.80%	1.09%
	90	top tray	0.03%	0.94%	0.46%	0.80%
IX2	68	bottom tray	0.03%	0.13%	0.09%	0.60%
	68	middle	0.03%	0.20%	0.09%	0.60%
	68	top tray	0.03%	0.11%	0.09%	0.60%
IX1	117	bottom tray	0.03%	0.73%	0.32%	0.80%
	117	middle	0.03%	1.25%	0.63%	0.84%
	117	top tray	0.03%	0.50%	0.21%	0.62%
IX2	108	bottom tray	0.03%	0.11%	0.09%	0.60%
	108	middle	0.03%	0.13%	0.09%	0.60%
	108	top tray	0.03%	0.11%	0.09%	0.60%

The concentration of nitrate over time can be seen in Figure 4-3. The final concentrations of nitric acid in the vessel were 11.4 M and 10.5 M for the IX1 and IX2 tests, respectively.

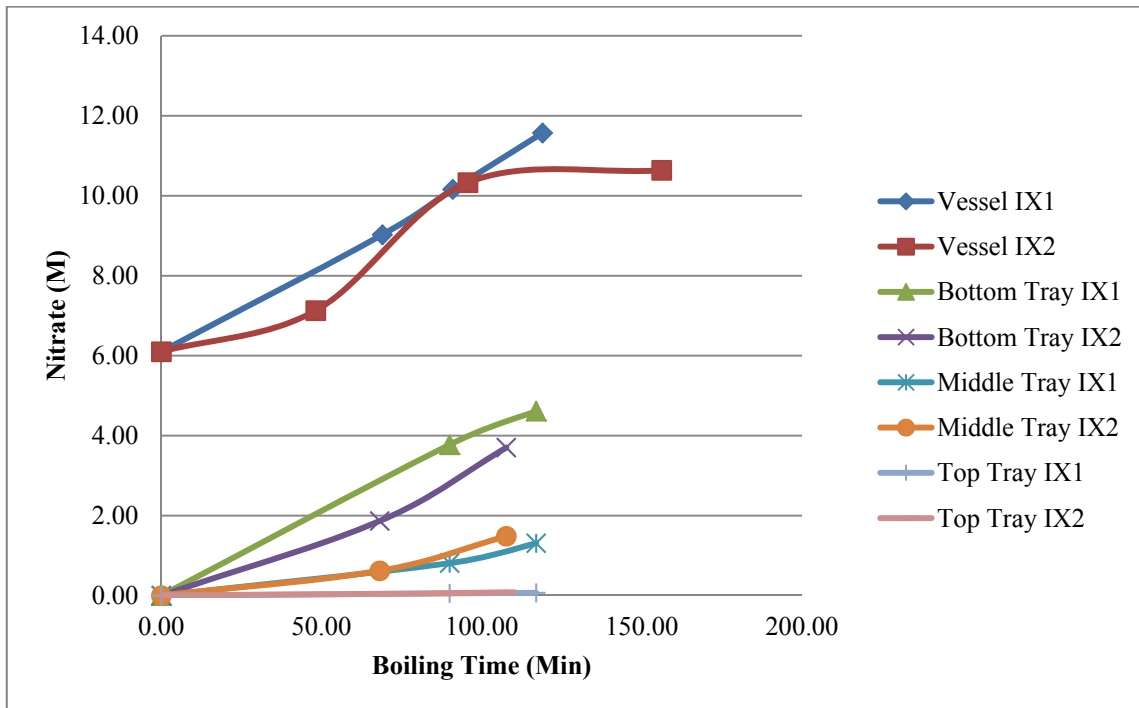


Figure 4-3. Nitrate Anion Concentrations within Fractional Distillation Column during IX1 and IX2 Raffinate Evaporation Tests

Mass losses were minimal, see Table 4-3, denoting that the condenser was relatively effective at the operating temperature (13-15 °C). Sources of variation impacting the results include analytical uncertainty, incompressible gases, and holdup within the vessel while draining.

Table 4-3. Mass Balance of Fractional Distillation

<u>Description</u>	<u>IX1 Run, g</u>	<u>IX2 Run, g</u>
Starting Mass in Vessel	977.7	968.5
Mass in Condenser at End	22.0	55.1
Mass in Trays at End	147.5	147.6
Mass in Vessel at End	606.8	604.9
Mass of Samples	166.5	145.3
Total Ending Mass	942.8	952.9
Unaccounted for Mass	34.9	15.6

4.2 Denitration with Formic Acid

Formic acid was added to the concentrated anion exchange raffinate simulant to reduce the nitrate concentration to ~1 M. Denitrification experiments were performed on 100 mL subsamples of the concentrated raffinate from the two test runs. The experimental parameters used for denitration can be seen in Table 4-4. It was determined that a formic acid addition speed greater than 0.35 mL/min would result in foam over when added to 100 mL of concentrated simulant in a 250 mL flask.

Table 4-4. Raffinate Formic Acid Denitration Experimental Parameters

<u>Starting Material</u>	<u>Experiment ID</u>	<u>Ratio of Formate Added to Starting Nitrate Conc.</u>	<u>Formic Addition Speed, mL/min</u>	<u>Stir Speed, RPM</u>	<u>Starting Nitrate Conc., M</u>	<u>Starting Density, g/mL</u>
IX1	NF1-1.05	1.03	0.13	200	11.57	1.31
IX1	NF1-0.85	0.83	0.13	200	11.57	1.31
IX1	NF1-0.70	0.67	0.13	200	11.57	1.31
IX1	NF1-0.90	0.87	0.30	200	11.57	1.31
IX2	NF1-0.88	0.87	0.13	200	10.64	1.31
IX2	NF1-0.88B	0.87	0.16	200	10.64	1.31
IX2	NF1-0.75	0.71	0.30	200	10.64	1.30
IX2	NF1-0.90B	0.89	0.35	300	10.64	1.31

The inception point for reaction and off-gassing in all tests was observed within 2-8 minutes. The hot plate was programmed was set to maintain a temperature of 90 °C; therefore, upon initiation of reaction the applied heat was regulated, as needed, to avoid uncontrolled temperature increase as a result of the exothermic reaction. The temperature was maintained between 88 °C and 94 °C. Samples were taken periodically to evaluate the change in nitrate concentration as the reaction proceeded (see Figure 4-4). It should be noted that NF1-0.85 likely proceeds exponentially, but a sample was not taken between 30 minutes and 245 minutes so the plotting program drew a straight line.

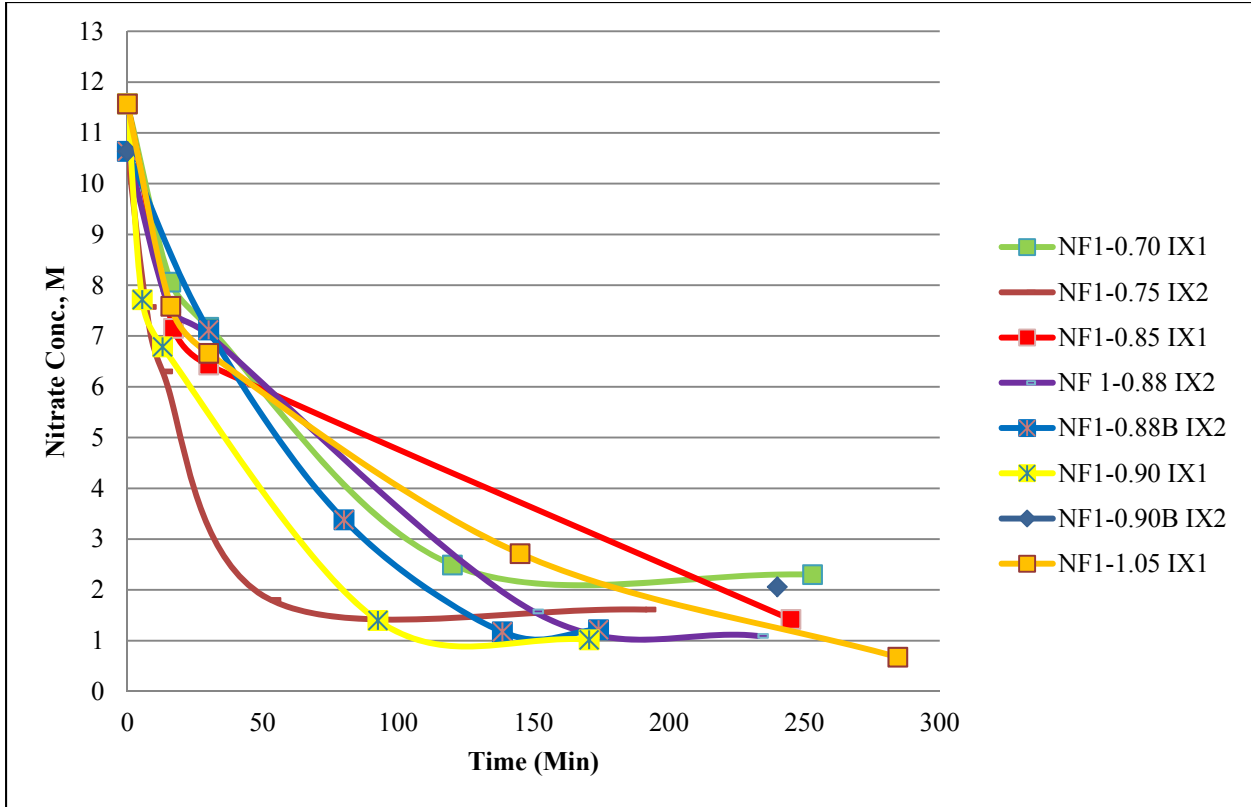


Figure 4-4. Raffinate Nitrate Anion Decomposition Results by Formic Acid Addition

It is seen that as the ratio of the moles of formic acid added per mole of nitrate increases, the final concentration of nitrate decreases, as expected. Results proceeded as expected based on the literature [7]. Reaction kinetics dictate that as the nitric acid concentration is decreased, the rate of reaction slows down. During nitrate destruction a significant amount of NO_x gases were visually observed in the vapor space. As the reaction proceeded, less NO_x was observed, but liquid vaporization was still apparent. Due to the large amount of gas evolved, a significant decrease in sample mass occurred. The 31% - 70% mass reduction assumed to be mass loss associated with the decomposition of nitric and formic acids. This was further investigated during the large scale run described in Section 4.6 Scaling Experiment.

Table 4-5. Mass Balance Results for Raffinate Denitration Runs

<u>Starting Material</u>	<u>Experiment ID</u>	<u>Initial Mass, g</u>	<u>Mass Added, g</u>	<u>Mass Removed from Sampling, g</u>	<u>Final Mass, g</u>	<u>Mass Loss, g</u>
IX1	NF1-1.05	131.00	65.70	25.51	57.43	113.76
IX1	NF1-0.85	130.26	52.80	30.26	33.03	119.77
IX1	NF1-0.70	130.46	42.91	29.68	42.45	101.24
IX1	NF1-0.90	130.19	55.57	21.07	41.70	122.99
IX2	NF1-0.88	130.60	52.90	29.83	47.39	106.29
IX2	NF1-0.88B	130.30	53.10	28.10	44.01	111.29
IX2	NF1-0.75	130.07	43.79	28.31	90.85	54.70
IX2	NF1-0.90B	130.57	52.14	7.46	120.65	54.60

Tests varied the ratio of formic acid added to the concentrated anion exchange raffinate. Results seen in Table 4-6 demonstrate that a molar ratio of formic to nitric acid greater than 0.90 is expected to destroy nitrate to a concentration of ~1 M or less, which is sufficiently low for effective precipitation of the target metals by the addition of oxalic acid.

Table 4-6. Results of Denitrification

<u>Starting Material</u>	<u>Experiment ID</u>	<u>Initial Nitrate Conc., M</u>	<u>Ratio of Initial Formate to Nitrate Conc.</u>	<u>Final Formate Conc., M</u>	<u>Final Nitrate Conc., M</u>	<u>Final Nitrite Conc., M</u>
IX1	NF1-1.05	11.57	1.03	4.94	0.68	< 0.002
IX1	NF1-0.85	11.57	0.83	1.25	1.42	< 0.002
IX1	NF1-0.70	11.57	0.67	0.03	2.30	< 0.002
IX1	NF1-0.90	11.57	0.87	2.18	1.02	< 0.002
IX2	NF1-0.88	10.64	0.87	1.48	1.09	< 0.002
IX2	NF1-0.88B	10.64	0.87	0.95	1.21	< 0.002
IX2	NF1-0.75	10.64	0.71	0.31	1.61	< 0.002
IX2	NF1-0.90B	10.64	0.89	2.06	1.30	< 0.02

The final residual formate concentration increases with the formate to nitrate ratio. The trends seen in Figure 4-5 can roughly be used to estimate the residual amount of formic and nitric acid after two hours of processing. A formate to nitrate ratio of ~0.90 is recommended because at this point nitrate is sufficiently low without the addition of excess formate.

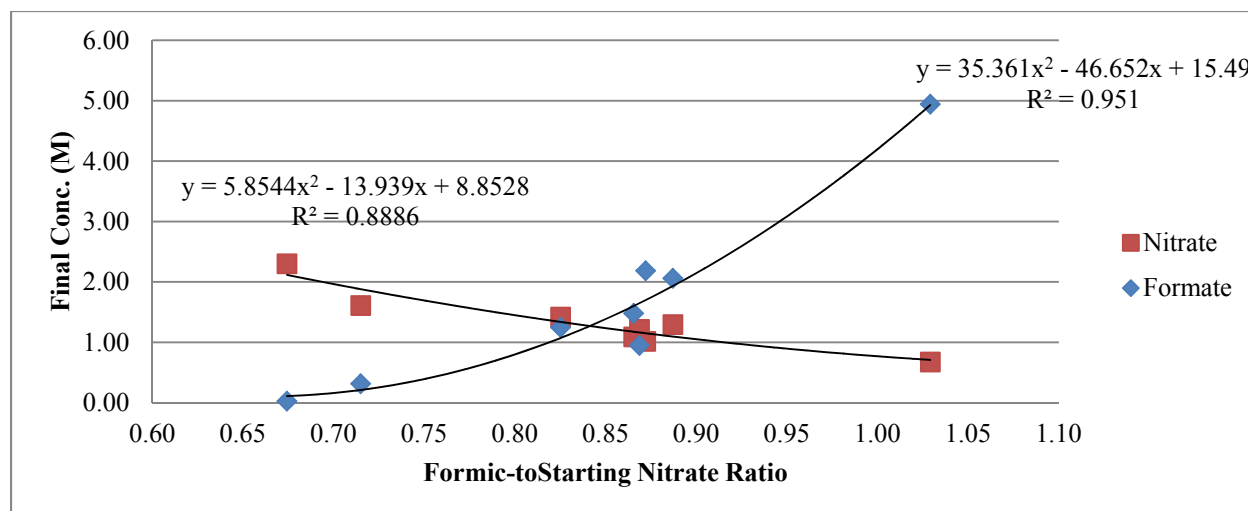


Figure 4-5. Final Formate and Nitrate Concentration Trends

4.3 Oxalate Precipitation

To better understand the precipitation kinetics a simple simulant was made to perform the oxalate precipitation tests. A 0.83 M oxalic acid solution was pumped into the simple simulant that was stirred at 300 rpm at the specified test temperature. Tests were allowed to digest for 2 or 4 hours as specified in Table 4-7.

The amount of oxalic acid added was varied for Test1 – Test 10. All tests were run in duplicate; therefore, Test 1 and 2 were intended to be the same conditions. For Tests 17 and 18, the addition of oxalic acid also contained isopropanol added to the oxalic acid at ~2 M. The final raffinate solution was ~7.5 vol% isopropanol for Test 17 and Test 18. Maintaining less than 24 vol% isopropanol is required for disposition to the HAD per L1 6.01 Rev. 27. For Tests 9 and 10, both simulant and oxalic acid were pumped simultaneously into 15 mL of the simulant to mimic continuous operations. Test 7 and Test 8 did not produce any significant precipitate. It is likely that an excess of 0.15 M oxalic acid is too low. Test 7 was filtered with a 0.45 μm disk (see 4.4 Filtration) to see if solids were visible once collected; however, no solids were seen on the filter. Thus, the solutions were sampled and an additional 0.05 M excess oxalic acid (final diluted concentration) was pumped into each and then allowed to digest for one hour. The unremediated Test 7 and 8 are denoted with the test number followed by the letter I to denote initial.

Table 4-7. Simple Simulant Oxalate Precipitation Conditions

<u>Test #</u>	<u>Sim. Vol., mL</u>	<u>Sim. Mass, g</u>	<u>Temp. °C</u>	<u>Initial Nitrate Conc., M</u>	<u>Initial Free Acid, M</u>	<u>Mass Formic Acid Soln Added, g</u>	<u>Mass Oxalate Soln. Added, g</u>	<u>Mass of Isopropanol Added, g</u>	<u>Oxalate Addition Speed, mL/min</u>	<u>Aging Time, Hr</u>
1	90	101.70	60	2.71	0.30	6.323	40.4	-	2.6	2
2	90	101.27	60	2.71	0.30	6.312	39.9	-	2.6	2
3	90	101.56	60	2.71	0.30	6.285	45.6	-	2.6	2
4	90	101.66	60	2.71	0.30	6.270	45.9	-	2.6	2
5	90	101.00	60	2.71	0.30	6.307	33.0	-	3.5	2
6	90	101.27	60	2.71	0.30	6.310	33.2	-	3.5	2
7I	90	100.84	60	2.71	0.30	6.311	22.3	-	2.6	4
7	90	100.84	60	2.71	0.30	6.311	32.3	-	2.6	1
8I	90	100.96	60	2.71	0.30	6.319	22.5	-	2.6	4
8	90	100.96	60	2.71	0.30	6.319	32.4	-	2.6	1
9	90	100.75	60	2.71	0.30	-	27.7	-	Cont.	2
10	90	101.84	60	2.71	0.30	-	35.6	-	Cont.	2
11	90	101.14	60	3.26	0.96	6.258	41.3	-	2.6	2
12	90	100.81	60	3.28	0.98	6.334	39.4	-	2.6	2
13	90	99.98	80	2.71	0.30	6.271	39.4	-	2.6	2
14	90	101.14	80	2.71	0.30	6.351	39.1	-	2.6	2
15	90	101.46	50	2.71	0.30	6.345	39.6	-	2.6	2
16	90	101.15	50	2.71	0.30	6.320	39.4	-	2.6	2
17	90	101.22	60	2.71	0.30	6.286	44.5	15.114	2.6	2
18	90	101.03	60	2.71	0.30	6.291	46.9	15.130	2.6	2
19	90	100.73	60	2.71	0.30	9.434	39.2	-	2.6	2
20	90	100.71	60	2.71	0.30	9.439	39.2	-	2.6	2

After filtering, the filtrate was sampled. IC results, seen in Table 4-8, show a decrease in the measured final nitrate and formate ion from the calculated final ion results that were expected. This decrease indicates that some denitration was occurring during oxalate precipitation. The formate result for 7I is slightly suspect, and likely higher given the results for Test 7, Test 8I, and Test 8. The oxalate results for Test 14, 15, and 16 are significantly lower than expected. Given that a satisfactory amount of oxalate was added in these tests and the precipitate produced was not especially significant (see Table A-7**Error! Reference source not found.** in 1.1.1.1Appendix A) the low oxalate results are likely an analytical error.

Table 4-8. IC Results of Simple Simulant Oxalate Precipitation Tests

<u>Test #</u>	<u>Calculated Final Nitrate, M</u>	<u>Measured Final Nitrate, M</u>	<u>Calculated Final Formate, M</u>	<u>Measured Final Formate, M</u>	<u>Oxalate Added, M</u>	<u>Oxalate Added Over Stoichiometry, M</u>	<u>Measured Final Oxalate Conc., M</u>	<u>Final Free Acid, M</u>
1	1.82	1.53	0.85	0.45	0.241	0.183	0.22	0.85
2	1.82	1.59	0.85	0.45	0.239	0.181	0.22	0.75
3	1.75	1.57	0.82	0.38	0.263	0.206	0.26	0.75
4	1.75	1.63	0.81	0.39	0.264	0.199	0.26	0.76
5	1.92	1.71	0.90	0.48	0.208	0.150	0.20	0.78
6	1.92	1.76	0.90	0.50	0.209	0.151	0.20	0.81
7I	1.93	1.98	0.90	0.48	0.153	0.094	0.13	1.08
7	1.93	1.90	0.90	0.67	0.154	0.146	0.22	1.02
8I	1.93	2.03	0.90	0.72	0.205	0.095	0.15	1.00
8	1.93	1.79	0.90	0.61	0.205	0.147	0.22	1.00
9	2.09	2.16	0.00	< 0.02	0.190	0.131	0.20	0.73
10	1.96	2.02	0.00	< 0.02	0.230	0.171	0.24	0.62
11	2.11	-	0.81	-	0.238	0.181	-	-
12	2.15	-	0.83	-	0.230	0.172	-	-
13	1.83	1.58	0.85	0.32	0.237	0.179	0.24	0.56
14	1.83	1.40	0.86	0.29	0.236	0.178	0.05 ⁷	0.55
15	1.83	1.40	0.86	0.34	0.238	0.180	0.03 ⁷	0.78
16	1.83	1.46	0.86	0.38	0.237	0.179	0.06 ⁷	0.85
17	1.58	-	0.74	-	0.231	0.173	-	-
18	1.55	0.90	0.73	0.69	0.240	0.182	0.27	0.74
19	1.80	1.34	1.26	0.51	0.231	0.174	0.20	0.64
20	1.80	-	1.26	-	0.232	0.174	-	-

The ICP-ES results were used to evaluate the selective precipitation of the metals from the solution. Dashed lines denote the calculated concentrations of the analytes within the test solution (Figure 4-6). Expected concentration is the dilution of the starting concentration as a result of the acid addition. The majority of analytical results for Al, Fe, and Mg in the filtrate are statistically similar to the feed concentration. Results indicate that precipitation of La and some Na is occurring. For Tests 11 and 12, the increased nitrate concentration appears to reduce selective precipitation.

⁷ The oxalate results for Test 14, 15, and 16 are significantly lower than expected and are likely an analytical error since a satisfactory amount of oxalate was added in these tests and the precipitate produced was not especially significant.

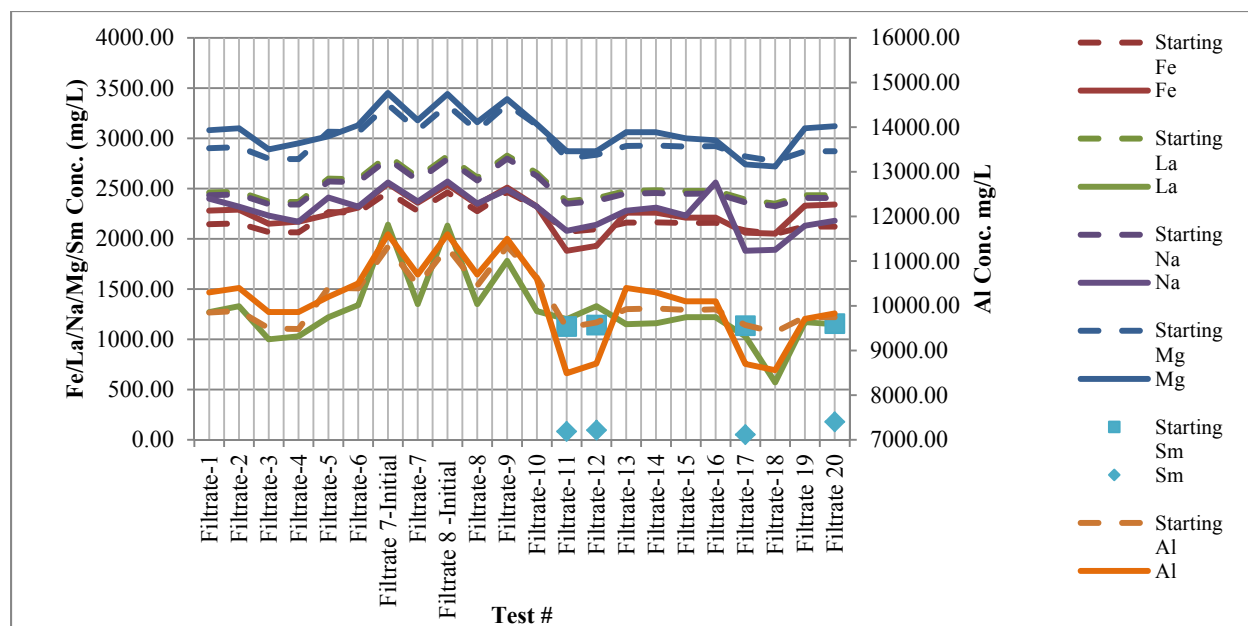


Figure 4-6. Metal Concentration Results of Oxalic Precipitation Filtrate of Simple Simulant

Decontamination factors, seen in Figure 4-7, indicate the impact of the experimental parameters on the selective precipitation of the rare earth and transuranic elements. The DF's in Figure 4-7 are averages of the two tests performed in duplicate (i.e. 1&2, 3&4, etc.). The use of isopropanol, in Tests 17 and 18, resulted in an increase in the precipitation of La and Sm, and a slight increase in the precipitation of undesired elements. Additional research may be needed to further investigate the use of isopropanol for selective oxalate precipitation. La is more difficult to precipitate than Sm. While additional formic acid was added in Test 19 and Test 20, the residual amount of formic acid for Test 19 indicated more significant degradation of formic than was observed in other tests. However, no formic acid was added to Tests 9 and 10 and comparing DFs with Test 19 and 20, which had additional formic, the formic acid concentration does not play a significant role influencing the DFs. Test 17 and 18 had isopropanol added unlike any of the other runs. Test 20 Sm DF is much less than Test 17 Sm DF so the isopropanol in Test 17 is impacting the Sm DF to the better. Tests 17 and 18 La DF is higher than Tests 19 and 20 again indicating that isopropanol increases the DF rare earth oxalates. Tests 1 and 2 have similar final nitrate and formate concentrations, along with similar amounts of added oxalic acid, to Tests 13 - 16. The main difference was the temperature of the solution. Tests 1 and 2 were conducted at 60 °C, while Tests 13 and 14 was at 80 °C, and Tests 15 and 16 was at 50 °C. No discernable trend is seen in the test results versus temperatures. In Tests 1 – 8 the amount of oxalic acid added was varied. In these tests it was observed that the La DFs increase relatively with the amount of oxalic acid added. Higher nitrate concentrations tend to have lower DFs for La based on the tests.

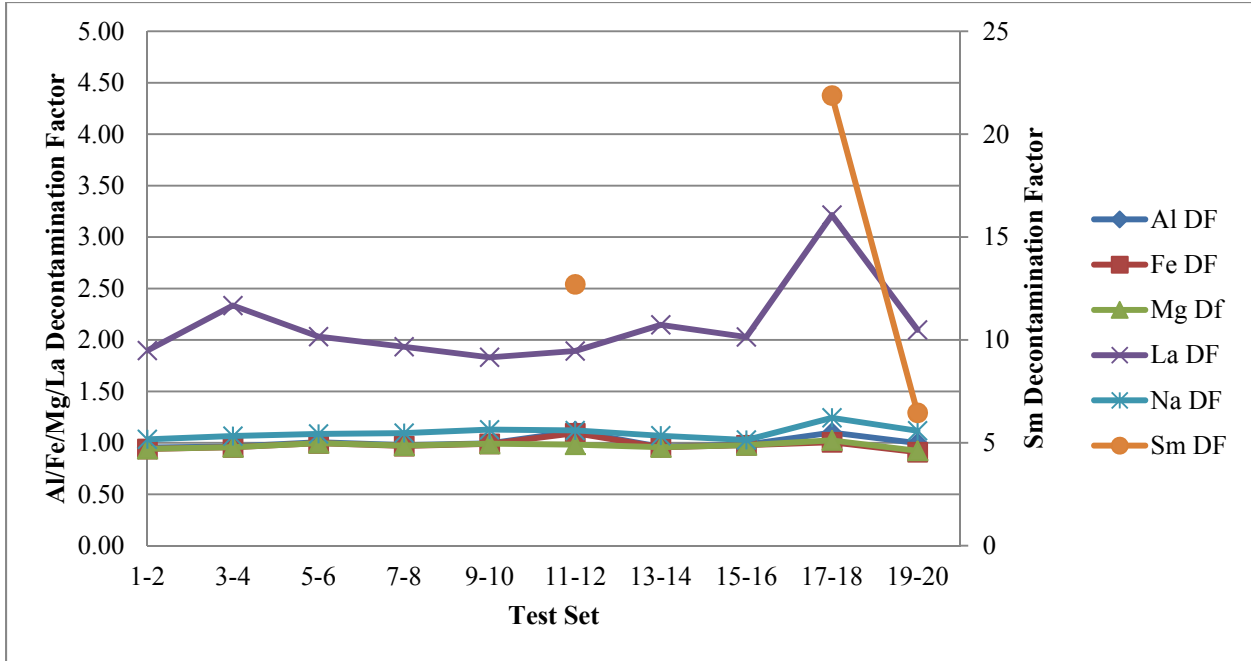


Figure 4-7. Decontamination Factors Observed for Simple Simulant Following Oxalate Precipitation

The average DF for each test set were plotted against the free acid and oxalic acid added as seen in Figure 4-7. The La DF seems to decrease with increasing free acid content, and increase with the amount of oxalate added.

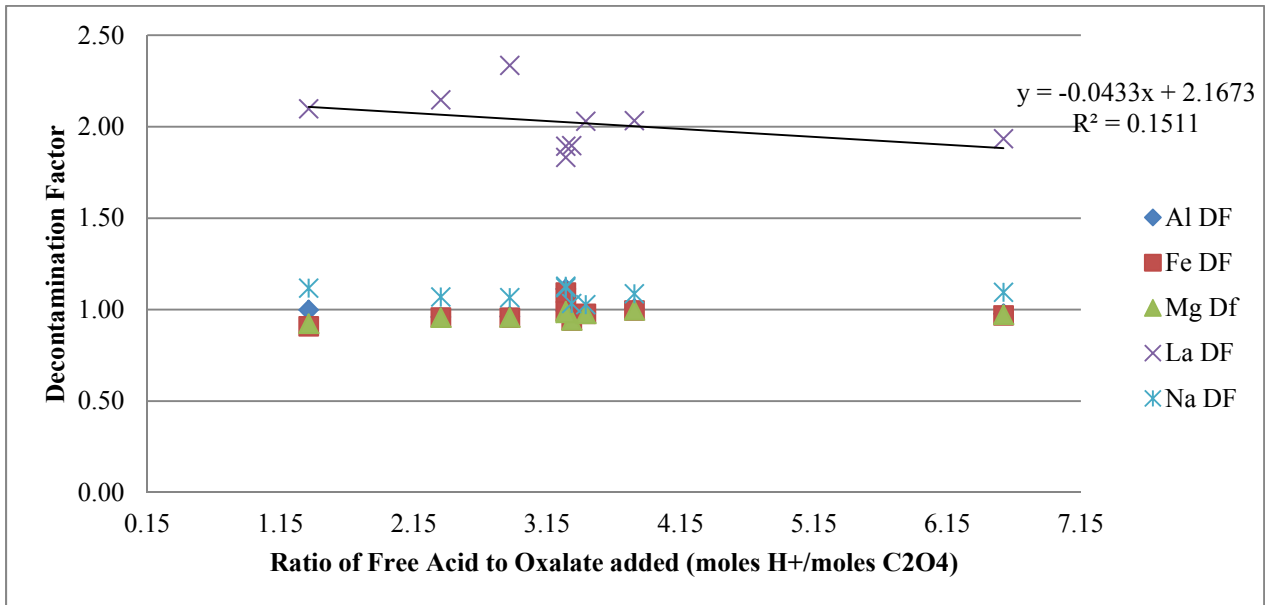


Figure 4-8. Decontamination Factor Trends Observed for the Simple Simulant Following Oxalate Precipitation

Oxalic acid was added to the denitrated anion exchange raffinate simulant as seen in Table 4-9 to precipitate metal oxalates. The target was 0.24 – 0.3 M of oxalic acid. The oxalic acid was pumped into the heated denitrated anion exchange raffinate, while stirring, by syringe pump.

Table 4-9. Complex IX Raffinate Simulant Oxalate Precipitation Experimental Conditions

<u>Exp. ID</u>	<u>Initial Vol. mL</u>	<u>Initial Mass, g</u>	<u>Initial Material</u>	<u>Temp., °C</u>	<u>Initial Nitrate Conc., M</u>	<u>Initial Formic, M</u>	<u>Initial Oxalate Conc. Added, M</u>	<u>Mass Oxalate Added, g</u>	<u>Stir Speed, RPM</u>	<u>Aging Time, Hr</u>	<u>Oxalate Addition Speed, mL/min</u>
NF1-0.70	28.88	32.60	IX1	60	3.37	0.11	0.83	16.76	300	2	2.61
NF1-0.75	32.24	35.40	IX2	60	2.05	0.38	0.83	16.84	300	2	2.61
NF1-0.85	47.07	48.59	IX1	60	0.682	0.271	0.83	16.87	300	2	2.61
NF1-0.88	42.59	51.91	IX2	70	0.98	1.33	0.55	46.09	250	2	1.5
NF1-0.88B	39.25	53.12	IX2	70	0.98	0.77	0.55	48.68	250	2	1.5
NF1-0.90	29.36	32.34	IX1	60	1.35	2.58	0.83	16.81	300	2	2.61
NF1-0.90B	41.81	46.03	IX2	60	1.30	2.06	0.83	20.46	300	2	1.3
NF1-1.05	47.20	52.87	IX1	70	0.68	4.94	0.55	36.85	250	2	1.5

As seen in Table 4-10, the expected and final nitrate and formate concentrations are fairly close. Thus, additional denitration does not seem to be occurring as was seen in the simple simulant tests, despite for some denitrated, concentrated anion exchange raffinate tests the initial formic acid concentration was higher. The nitrate concentration results of NF1-0.70 are a lower than expected, which may be a result of analytical uncertainty.

Table 4-10. IC Data for Complex IX Raffinate Oxalate Precipitation Tests

<u>Exp. ID</u>	<u>Initial Nitrate Conc., M</u>	<u>Calculated Final Nitrate, M</u>	<u>Measured Final Nitrate, M</u>	<u>Initial Formate Conc., M</u>	<u>Calculated Formate, M</u>	<u>Measured Final Formate, M</u>	<u>Oxalate Added, M</u>	<u>Oxalate Added Over Stoichiometry, M</u>	<u>Measured Final Oxalate Conc., M</u>
NF1-0.70	2.30	2.16	1.71	0.03	0.07	0.02	0.30	0.14	0.17
NF1-0.75	1.61	1.36	1.23	0.31	0.25	0.16	0.28	0.11	0.14
NF1-0.85	1.42	0.51	0.41	1.25	0.20	0.18	0.21	0.04	0.15
NF1-0.88	1.09	0.50	0.60	1.48	0.68	0.61	0.27	0.14	0.24
NF1-0.88 B	1.21	0.49	0.72	0.95	0.39	0.34	0.27	0.15	0.25
NF1-0.90	1.02	0.87	0.75	2.18	1.66	1.38	0.30	0.14	0.23
NF1-0.90 B	1.30	0.88	0.84	2.06	1.40	1.30	0.27	0.10	0.20
NF1-1.05	0.68	0.38	0.30	4.94	2.79	2.71	0.24	0.10	0.21

The filtrate results, as seen in Table 4-11, indicate that Al, Fe, Mg, Mo, Na, and Sb consistently remain in solution. Percent solubility is defined as the ratio of the measured concentration in the filtrate (soluble species) to the expected concentration of the constituent in the filtrate assuming it all remains soluble. The initial Fe results for NF1-0.85 were low (446 mg/L) after denitration. There were considerable solids in the starting solution, which likely were precipitated iron. Filtrate results indicate that Eu, Gd, La, Nd, Pr, Ru, Sm, and Zr precipitate from solution, presumably as oxalate salts. Small amounts of Sr may also precipitate.

Table 4-11. Metal Concentrations in the IX Raffinate Filtrate Following Oxalate Precipitation

Metal	% of Calculated Final Concentration							
	NF1-0.70	NF1-0.75	NF1-0.85	NF1-0.88	NF1-0.88B	NF1-0.90	NF1-0.90B	NF1-1.05
Al	105%	103%	104%	109%	134%	104%	103%	112%
Ce	12%	10%	3%	4%	4%	6%	6%	4%
Eu				0%	0%			0%
Fe	104%	106%	197%	113%	138%	103%	103%	114%
Gd				0%	0%			0%
La	29%	27%	12%	16%	18%	19%	20%	16%
Mg	103%	102%	101%	103%	125%	104%	103%	102%
Mo	105%	159%		108%	129%	101%	183%	105%
Na	100%	101%	100%	82%	129%	102%	101%	103%
Nd				0%	1%			0%
Pr				1%	2%			1%
Re				101%	118%			106%
Ru				2%	2%			2%
Sb	156%	150%	135%			155%	147%	
Sm				0%	0%		0%	0%
Sr	96%	95%	95%	104%	124%	97%	96%	103%
Zr				54%	83%			85%
Zn	103%	103%	101%	94%	96%	104%	103%	103%

Again, it is seen that La is more difficult to precipitate selectively than the other rare earths tested. The difficulty of precipitation appears to be Eu < Sm < Gd < Nd < Pr < Ru < Ce < La. The DFs can be seen in Table 4-12. The increased nitrate concentrations in NF1-0.70 and NF1-0.75 likely lead to a lower DF for La and Ce.

Table 4-12. Metal Decontamination Factors for the Complex IX Raffinate Following Oxalate Precipitation

	<u>NF1-0.70</u>	<u>NF1-0.75</u>	<u>NF1-0.85</u>	<u>NF1-0.88</u>	<u>NF1-0.88B</u>	<u>NF1-0.90</u>	<u>NF1-0.90B</u>	<u>NF1-1.05</u>
Al	0.96	0.97	0.96	0.91	0.75	0.96	0.97	0.89
Ce	8.37	9.82	35.15	27.23	22.55	16.43	15.45	25.61
Eu				1435	896.2			1410
Fe	0.97	0.94	0.51	0.89	0.73	0.97	0.97	0.87
Gd				421.4	313.4			416.5
La	3.44	3.64	8.58	6.29	5.55	5.26	4.89	6.28
Mg	0.97	0.98	0.99	0.97	0.80	0.96	0.97	0.98
Mo	0.95	0.63		0.93	0.77	0.99	0.55	0.95
Na	1.00	0.99	1.00	1.22	0.77	0.98	0.99	0.97
Nd				252.6	169.6			204.8
Pr				83.20	62.63			76.51
Re				0.99	0.85			0.95
Ru				45.93	40.68			56.48
Sb	0.64	0.66	0.74			0.64	0.68	
Sm				1370	865.3		302.7	1262
Sr	1.05	1.06	1.06	0.96	0.80	1.03	1.04	0.97
Zr				1.84	1.21			1.18
Zn	0.97	0.97	0.99	1.06	1.04	0.97	0.97	0.97

In comparing the DFs for La and Ce to the nitrate, formate, and amount of oxalate added, it is clearly seen that the starting nitrate concentration more substantially affects the metal DF, while the starting formate concentration has little impact. As the starting nitrate goes from 3.5 to 0.7 M in Figure 4-9 the DF of Ce increases ~4x and the DF of La increases ~2x.

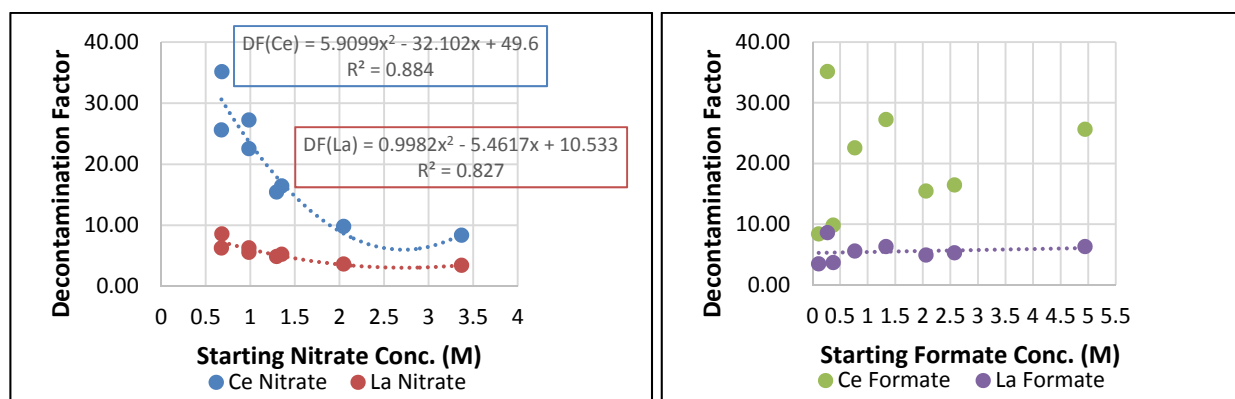


Figure 4-9. DF Trends for the Complex IX Raffinate Filtrate Following Oxalate Precipitation

The DF trends could be utilized to predict the expected metal DFs given the oxalate addition and the starting nitrate concentration. However, to combine the added oxalate and starting nitrate factors into one function to predict DF would be difficult as more data points would be needed to fully define the relationship.

4.4 Filtration

Clean filters were calcined in air at 1000 °C in clean, glazed alumina crucibles to determine ash content. All crucibles were empty (no ash content) after calcination, except the crucibles containing the cellulose nitrate filter, which contained black specs (ash).

Table 4-13. Ash Content of Filter

<u>Filter Type</u>	<u>Size, mm</u>	<u>Filter Mass, g</u>	<u>Mass After Calcination, g</u>
CN	90	0.581	0.002
CN	90	0.389	0.000
PP	47	0.036	0.000
PP	47	0.035	0.000
PC	90	0.115	0.000

Filter disks were also evaluated for resistance to nitric acid. The polypropylene (PP), polycarbonate (PC), and cellulos nitrate (CN) filter disks were observed to be intact and could be handled with tweezers after soaking in 3.9 M nitric acid for two weeks. Therefore, PP and PC were down selected for additional testing with the simple simulant.

Two 47 mm hydrophilic filter disks were evaluated using slurries produced from the oxalate precipitation tests. Filter pore sizes were: 0.45 µm PP and 0.4 µm PC. Each precipitate slurry was poured over the filter disk and collected in two to four 60 mL centrifuge tubes.

Table 4-14. Mass Balance Data from Simple Simulant Oxalate Precipitation Slurries

<u>Test #</u>	<u>Total Initial Mass, g</u>	<u>Filtrate Total Mass, g</u>	<u>Variance in Mass, g</u>	<u>Wet Precipitate Weight + Filter Paper, g</u>
1	148.43	135.91	12.51	0.621
2	147.48	136.97	10.51	0.681
3	153.45	143.79	9.66	0.728
4	152.03	145.50	8.33	0.736
5	140.31	138.13	2.17	0.134
6	140.78	137.77	3.01	0.036
7	139.44	110.25	29.20	0.736
8	139.69	114.03	25.66	0.697
9	128.48	124.34	4.13	0.043
10	137.48	132.69	4.79	0.029
11	154.35	142.36	11.99	0.328
12	152.33	147.56	4.78	0.230
13	145.68	111.26	34.43	0.674
14	146.58	138.98	7.61	0.595
15	147.37	142.12	5.25	0.637
16	146.90	142.98	3.92	0.575
17	167.11	153.40	13.71	0.671
18	169.37	155.12	14.25	0.938
19	149.34	156.29	6.72	0.519
20	149.35	142.99	6.36	0.494

Filtration was quick and no problems were observed during filtration. It was observed that precipitation within the filtrate solutions continues to occur. Therefore, for Test 1 the filtrate was refiltered to remove the solids, and a sample of the clarified filtrate sent for analysis. Results, seen in Table 4-15, indicate that the concentrations of several metals other than the targets metals decrease over time. Therefore, it is recommended to filter the material immediately after the oxalic acid strike to prevent excess, unwanted solids from forming.

Table 4-15. Metal Concentrations in the First and Second Filtrate Products from Test 1

<u>Filtrate</u>	<u>Al, mg/L</u>	<u>Fe, mg/L</u>	<u>La, mg/L</u>	<u>Mg, mg/L</u>	<u>Na, mg/L</u>
Test 1- 1 st Filtration	10300	2280	1270	3080	2400
Test 1 2 nd Filtration	10200	2270	1270	3070	2240

Some wash solutions were analyzed to see if certain soluble elements, like sodium, could be washed from the precipitate. The metal concentrations are provided as percentages of the original calculated values in Table 4-16. There is no discernable trend in Na; however, it is expected that Na can be rinsed out of the wet cake if it were to precipitate. Prior to rinsing the wet cake the vacuum pump was started. Each time a small amount of filtrate was expelled from the filter housing. The percent of Al and Fe appear relatively

close to one another, which is likely a result of the equal carryover of the filtrate. Mg is consistently lower, which may indicate that Mg precipitates in the wash.

Table 4-16. Wash Solutions

Metal	% of Initial Calculated Concentration										
	Wash-1	Wash-2	Wash-3	Wash-4	Wash-5	Wash-6	Wash-7	Wash-13	Wash-14	Wash-15	Wash-16
Al	6.1%	3.6%	12.2%	6.1%	14.0%	16.9%	13.4%	18.8%	8.5%	13.4%	7.7%
Fe	6.2%	3.7%	12.5%	6.3%	14.6%	17.4%	13.9%	19.3%	8.8%	13.9%	8.1%
Mg	4.5%	4.2%	10.9%	4.7%	12.8%	15.8%	12.0%	17.6%	7.3%	12.2%	6.6%
La	1.1%	0.6%	1.1%	0.8%	1.1%	1.4%	1.6%	1.5%	0.9%	1.2%	0.8%
Na	9.9%	4.4%	12.2%	6.5%	12.1%	14.2%	10.9%	16.1%	7.1%	10.7%	6.1%

Filtration was equally quick for the precipitated complex anion exchange raffinate. Mass balance information for these tests is provided in Table 4-17.

Table 4-17. Mass Balance Data from Complex IX Raffinate Oxalate Precipitation Slurries

Experiment ID	Total Initial Mass, g	Filtrate Total Mass, g	Variance in Mass, g	Wet Precipitate Weight + Filter Paper, g
NF1-0.70	49.361	46.24	3.12	0.550
NF1-0.75	52.239	48.79	3.44	0.634
NF1-0.85	65.462	63.87	1.59	0.447
NF1-0.88	98.001	90.98	7.02	1.369
NF1-0.88B	101.804	93.87	7.94	1.636
NF1-0.90	49.150	44.78	4.37	0.639
NF1-0.90B	66.823	56.28	10.54	0.925
NF1-1.05	89.715	82.17	7.55	0.790

Deviation in the mass balance could be a result of hold up during transferring, mass loss to the vapor space, or filtrate held up in the filter housing that was transferred into the wash.

4.5 Calcination

The simple simulant filtered metal oxalate solids were combined and calcined as shown in Table 4-18. Crucibles 3 and 4 were sent for analysis by TGA.

Table 4-18. Simple Simulant Calcined Data

<u>Crucible</u>	<u>Filter Type</u>	<u>Test #s Calcined</u>	<u>Wet Precipitate Weight + Filter Paper, g</u>	<u>Calcined Weight, g</u>
1	PP	2, 13, 15, 7B	2.728	1.146
2	PC	1, 14, 16, 8	2.488	1.095
3	PP	3, 5, 7, 11, 9, 19	1.800	0.717
4	PC	4, 6, 12, 10, 20	1.525	0.648

Calcination conditions: 1000 °C, in air, 2 hrs.

TGA results indicated that Crucible 3 was above the weight loss limit of 0.5 wt% (Figure 4-10), and Crucible 4 was below the weight loss limit (Figure 4-11). The variation in the TGA measurements is not significant enough to determine if it was due to the difference in filter material or differences in the oxide content. The calcined solids were dissolved by peroxide fusion, thus the sodium content could not be measured. Elemental analysis results can be found in Table 4-19 below.

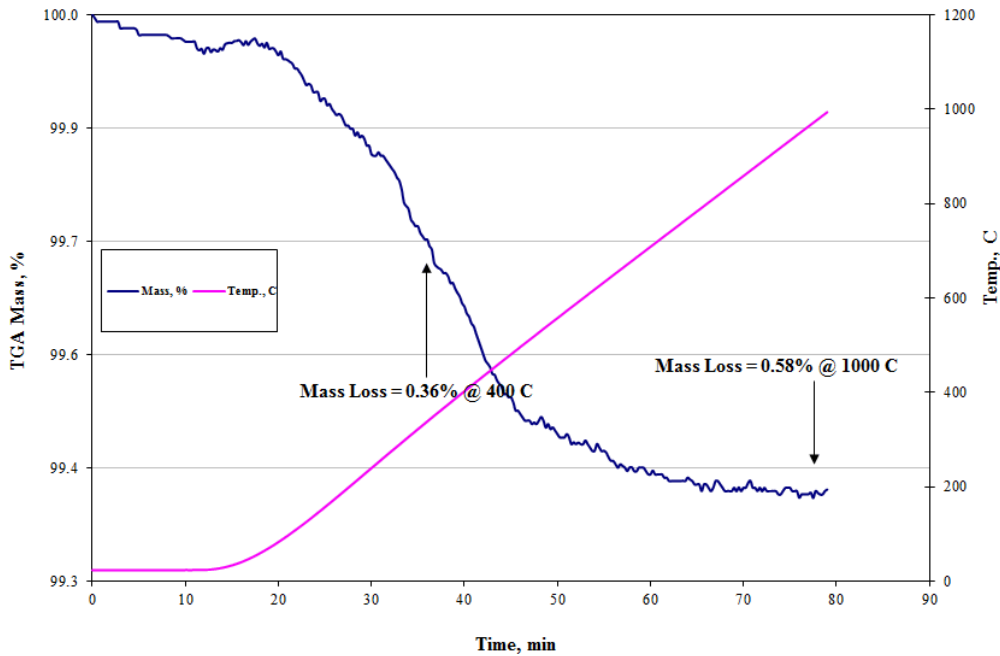


Figure 4-10. TGA Results for Crucible 3 (PP) Containing Metal Oxides Product

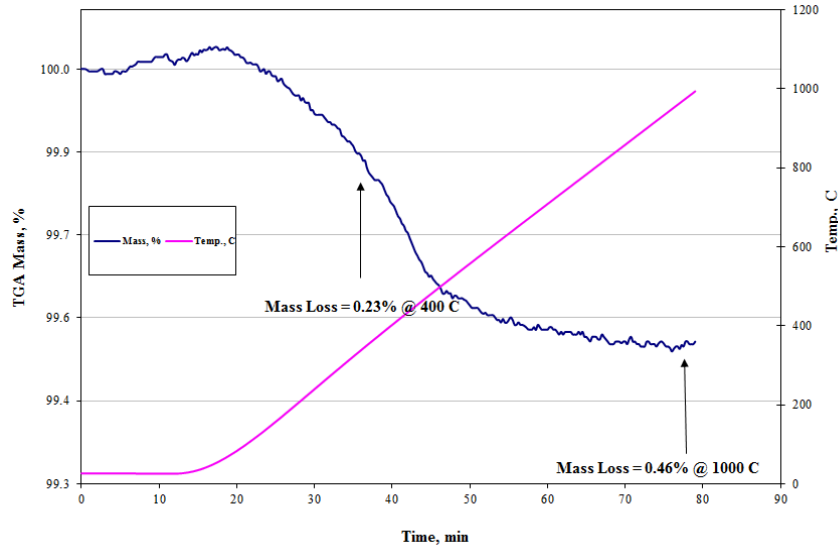


Figure 4-11. TGA Results for Crucible 4 (PC) Containing Metal Oxides Product

Table 4-19. Elemental Composition of Calcined Simple Simulant Metal Oxides

<u>Metal</u>	<u>µg/g Calcined Solids</u>			
	<u>Crucible 1</u>	<u>Crucible 2</u>	<u>Crucible 3</u>	<u>Crucible 4</u>
Al	< 347	< 1910	< 2980	< 210
Fe	736	< 1140	2330	456
Mg	< 2070	< 1140	1960	< 125
La	330,000	296,000	302,000	316,000
Sm	507000	467000	509,000	527,000
Carbon	-	-	548	631

The calcined anion exchange raffinate can be seen in Table 4-20. The total mass reduction is 99.6 – 99.9%.

Table 4-20. Complex IX Raffinate Oxalate Precipitate Calcination Results

<u>Experiment ID</u>	<u>Wet Precipitate Weight + Filter Paper, g</u>	<u>Calcined Weight, g</u>	<u>Filter Type</u>
NF1-0.70	0.550	0.232	PC
NF1-0.75	0.634	0.285	PC
NF1-0.85	0.447	0.197	PC
NF1-0.88	1.369	0.364	PC
NF1-0.88B	1.636	0.358	PC
NF1-0.90	0.639	0.264	PP
NF1-0.90B	0.925	0.494	PC
NF1-1.05	0.790	0.341	PP

Calcination conditions: 1000 °C, in air, 2 hrs.

The TGA spectra results for the calcined solids from various samples are provided in Figure 4-12 through Figure 4-14. The data shows a mass loss of ~1.5 wt% - 2 wt%. Majority of the mass loss occurs at a temperature greater than 450 °C. TGA-MS detected very small amounts of H₂O, CO₂ and NO₂ (Figure 4-15 and Figure 4-16), thus the mass loss was likely the vaporization of one of the oxides.

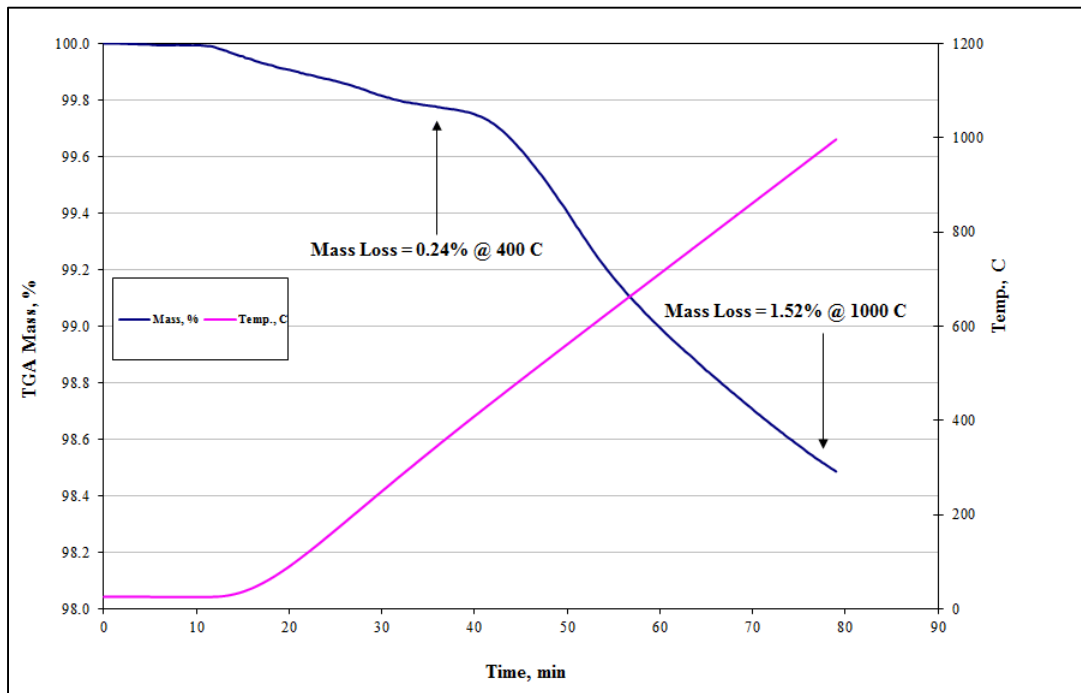


Figure 4-12. TGA Spectra for the Residual Metal Oxide Product of NF1-0.90

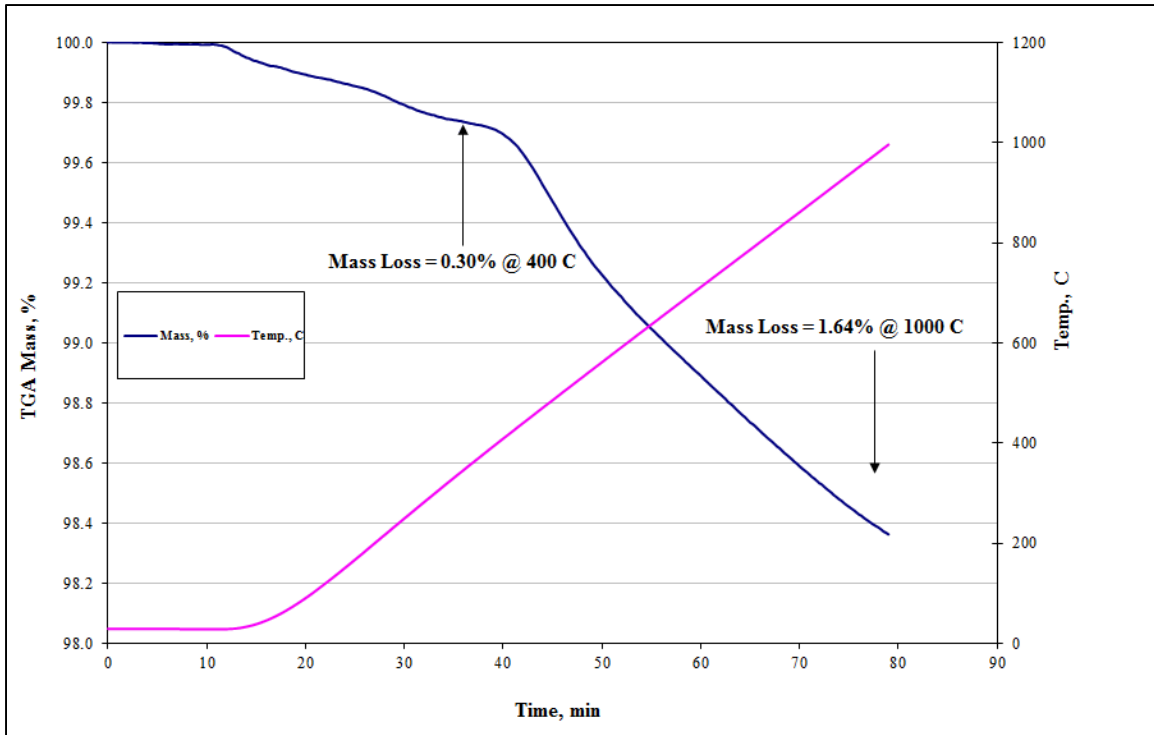


Figure 4-13. TGA Spectra for the Residual Metal Oxide Product of NF1-0.70

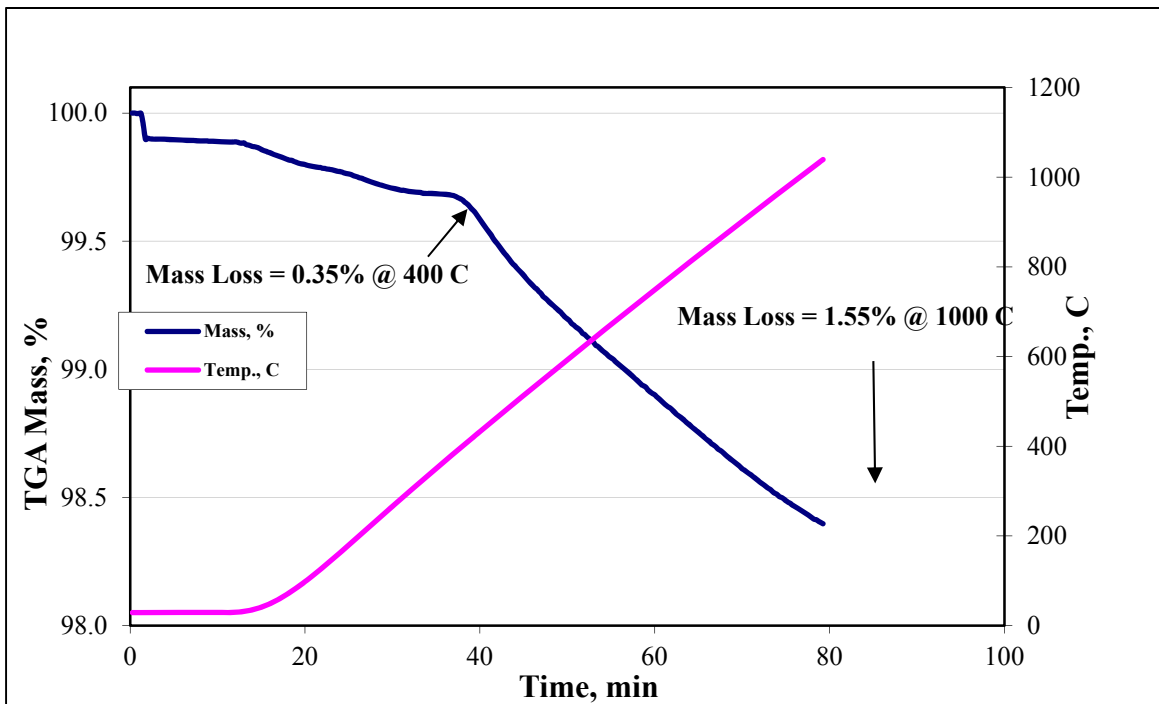


Figure 4-14. TGA Spectra for the Residual Metal Oxide Product of NF1-0.90B

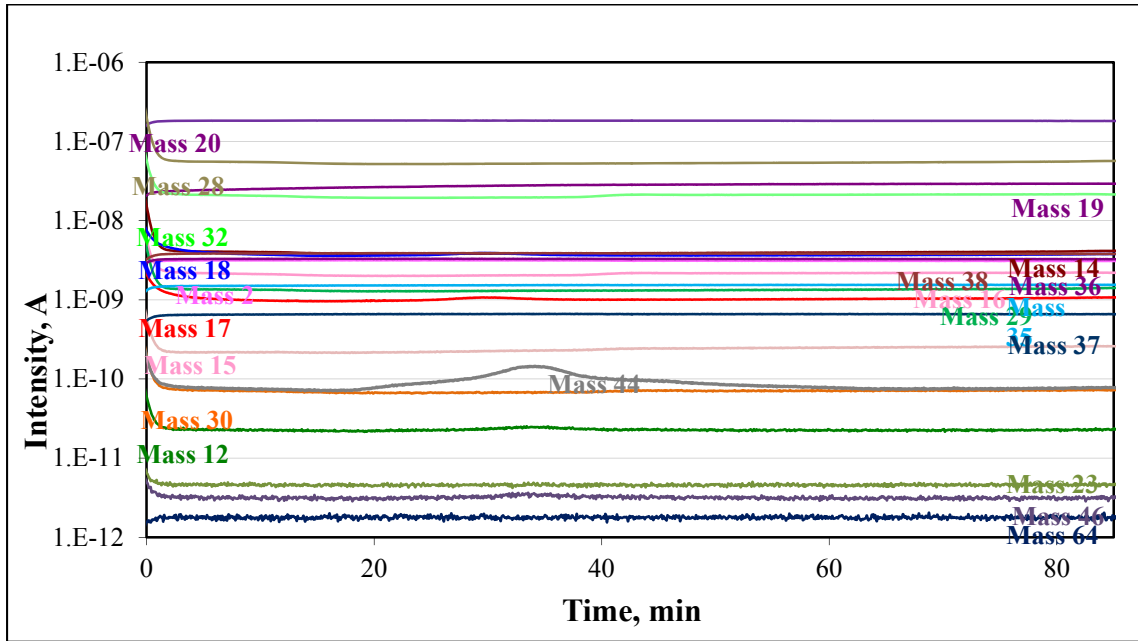


Figure 4-15. Mass Spectrometry data for TGA off gas of NF1-0.90B

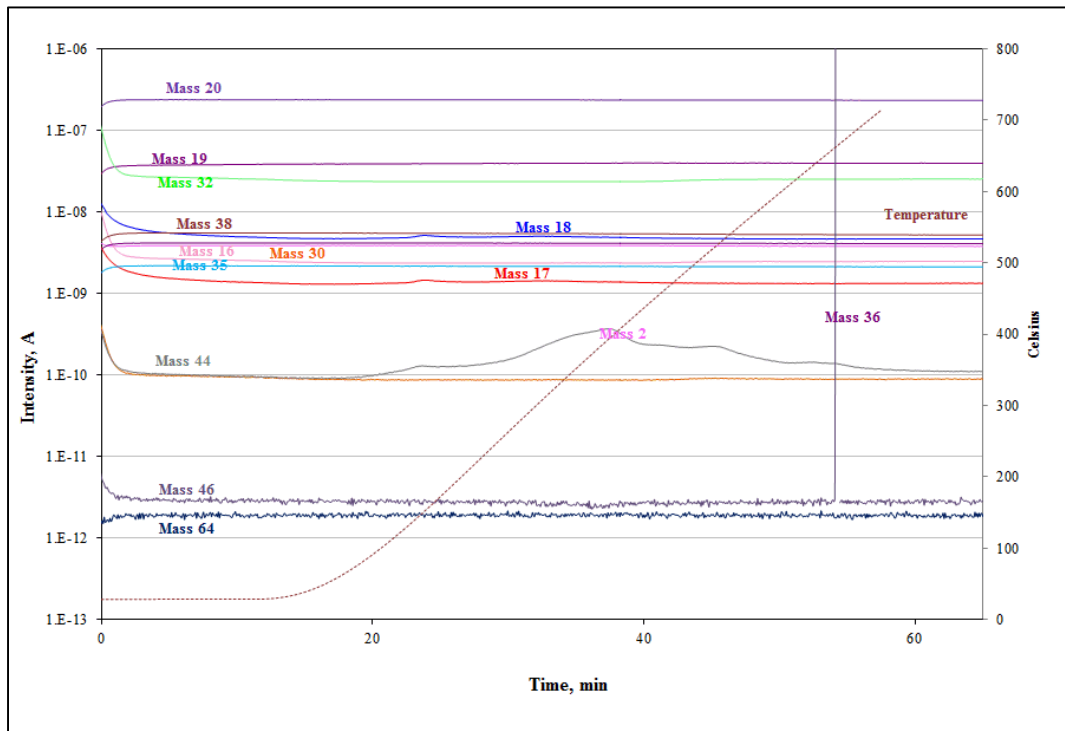


Figure 4-16. Mass Spectrometry Results of TGA Off Gas for NF1-0.88

The residual metal oxides formed from calcining the oxalic acid precipitate were dissolved by peroxide fusion and analysis results for several samples are seen in Table 4-21.

Table 4-21. Calcined Anion Exchange Raffinate

<u>Metal</u>	<u>Oxide Form</u>	<u>Element to Oxide Conversion Factor</u>	<u>NF1-1.05</u>		<u>NF1-0.88</u>		<u>NF1-0.90B</u>	
			<u>µg/g</u>	<u>Oxide wt%</u>	<u>µg/g</u>	<u>Oxide wt%</u>	<u>µg/g</u>	<u>Oxide wt%</u>
Al	Al ₂ O ₃	1.889	< 1790	< 0.35%	< 1450	< 0.28%	< 242	< 0.05%
Mg	MgO	1.658	< 107	< 0.02%	< 86.9	< 0.01%	<145	<0.03%
Sn	SnO ₂	1.270	< 5900	< 0.77%	< 4790	< 0.62%	<797	<0.11%
Zn	ZnO	1.245	< 267	< 0.03%	< 216	< 0.03%	<371	<0.05%
Fe	Fe ₂ O ₃	1.430	653	0.10%	360	0.05%	952	0.14%
Sr	SrO	1.183	125	0.02%	150	0.02%	168	0.02%
Ru	RuO ₂	1.158	< 0.901	< 0.00%	0.978	0.00%	< 3.041	0.00%
Pd	PdO	1.150	955.00	0.11%	1970	0.23%	3039	0.37%
Cs	Cs ₂ O	1.060	29.2	0.00%	29.6	0.00%	36.6	0.00%
La	La ₂ O ₃	1.173	40300	4.83%	40900	4.88%	34754	4.26%
Ce	Ce ₂ O ₃	1.171	132000	15.81%	134000	15.97%	127264	15.58%
Pr	Pr ₂ O ₃	1.170	335000	40.10%	336000	40.00%	330931	40.48%
Nd	Nd ₂ O ₃	1.166	171000	20.40%	172000	20.41%	169745	20.69%
Sm	Sm ₂ O ₃	1.160	35200	4.17%	35400	4.18%	34776	4.21%
Eu	Eu ₂ O ₃	1.158	24500	2.90%	24300	2.86%	24775	3.00%
Gd	Gd ₂ O ₃	1.153	88100	10.39%	89200	10.46%	91430	11.01%
Re	ReO ₂	1.172	9.36	0.00%	3.93	0.00%	6.76	0.00%
Sum				97.8%		98.3%		95.68%

Calculation of the data provided in Table 4-21 involved the assumption that all metals are in the oxide form, since the material was calcined to 1000 °C. It is possible that sodium or another residual component is responsible for or contributing to the mass loss. Calcining the material longer, or using a forced airflow would likely drive off the volatile species; however, testing is needed to confirm this.

4.6 Scaling Experiment

A single, large laboratory-scale experiment was performed to demonstrate the feasibility of separating the desired metal product (in oxide form) from the waste on a semi-continuous scale. This was performed to aid in developing scaling factors.

A 1.5 L scale experiment was performed using anion exchange raffinate simulant. One liter of anion exchange raffinate #2 (IX2) was added to the evaporator vessel. The mixer was set to 500 RPM and the chiller to 15 °C. Two heating rods with a diameter of 3/8" and a heated length of 2" had power of 250W were used to heat the solution. This resulted in an average boilup rate of 10.9 g/min of condensate collected. After collecting ~355 grams of liquid, the condensate was sampled and the FMI pump was used to add an additional 500 mL of IX2 simulant from below the liquid surface, simulating continuous operations. The average flowrate of the FMI pump during the addition was 12.0 mL/min (14.5 g/min). The average boilup rate after beginning continuous operations was 10.8 g/min. After removing a total of 916 grams of condensate solution, a new storage bottle was used to collect the next 418 g of condensate.

The second portion of the condensate was expected to contain nitric acid vapor (azeotropic boiling). The heating profile during the large scale test can be seen in Figure 4-17. Samples were taken periodically from each set of condensates.

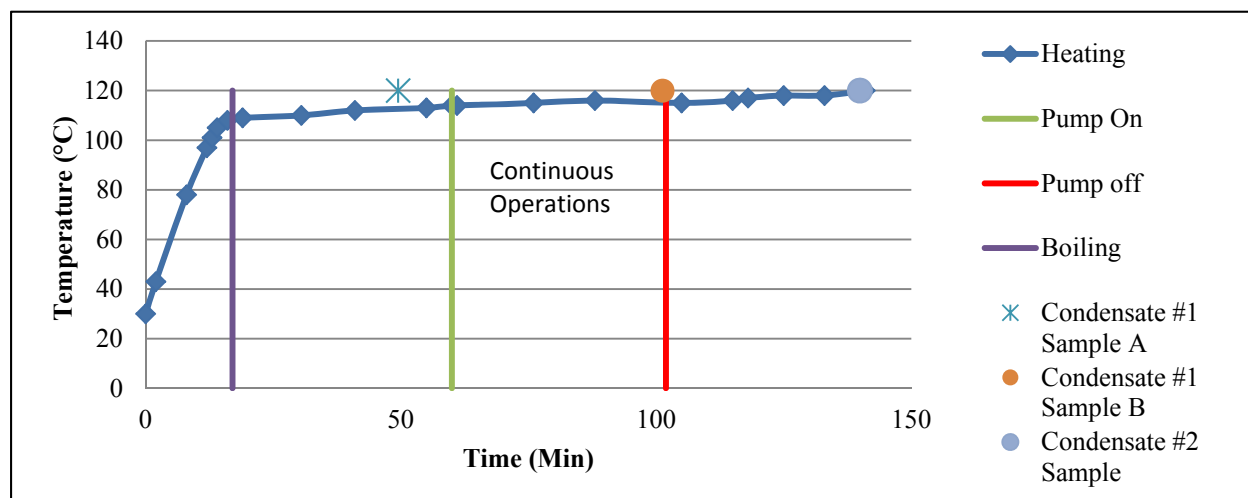


Figure 4-17. Temperature Profile during Large Scale IX Raffinate Evaporation

After completing the evaporation, the experiment was stopped and the equipment was allowed to cool overnight. Liquid that collected in the condensate collection tank during cooling was drained and sampled. Results can be seen in Table 4-22. The results for the final raffinate simulant in the vessel correspond to the concentrated anion exchange raffinate. The initial measured IX2 simulant nitrate ion concentration was 6.1 M based on analysis. The nitrate anion and free acid concentrations in the first condensate sample analyzed were low (< 1 M). The nitrate anion and free acid concentrations in the second condensate sample were moderate (2.3-2.6 M) indicating the onset of azeotropic boiling and the carryover of more nitric acid to the condensate. During full azeotropic boiling (acid rich cut) the nitrate anion and free acid concentrations were high (8.5-9.5 M) in the condensate. The condensate collecting during cooling was even higher in nitrate anion and acid (10.6-11.3 M). The final concentrated simulant in the evaporator pot contained the highest nitric acid concentration (11.4-14.7 M).

Table 4-22. Large Scale IX Raffinate Evaporation Data

	<u>Initial Anion Exchange Raffinate Simulant</u>	<u>Condensate Removed Prior to Starting Continuous Operations</u>	<u>Total Condensate Removed during Dewater Operations</u>	<u>Total Condensate Removed during Azeotropic Boiling</u>	<u>Condensate Collected during Cooling</u>	<u>Final Concentrated Raffinate Simulant</u>
Simulant or Condensate Mass, g	1818 ⁸	355	916	418	16	468
Density, g/mL	1.20	1.03	1.08	1.27	1.31	1.44
Free Acid, M		0.78	2.35	8.50	10.60	11.40
Formate, M		< 0.022	< 0.022	< 0.022	< 0.022	< 0.022
Nitrite, M		< 0.022	< 0.022	< 0.022	< 0.022	< 0.022
Nitrate, M	6.10	0.876	2.55	9.32	11.26	14.69
Oxalate, M		< 0.011	< 0.011	< 0.011	< 0.011	< 0.011
Al, mg/L	3,718	< 48.2	< 48.2	< 48.2	< 48.2	18400
Ce, mg/L	573	< 0.401	< 0.401	0.631	2.07	374
Cs, mg/L	225	0.003	0.006	0.410	1.521	922
Fe, mg/L	943	< 20.4	< 20.4	< 20.4	< 20.4	4420
La, mg/L	178	< 0.902	< 0.902	< 0.902	< 0.902	161
Mg, mg/L	1,078	< 2.17	< 2.17	< 2.17	< 2.17	2910
Mo, mg/L	83.8	< 8.62	< 8.62	< 8.62	< 8.62	353
Na, mg/L	167	< 5.08	< 5.08	< 5.08	< 5.08	744
Sm, mg/L	126	< 0.01	< 0.01	0.14	0.486	441
Sn, mg/L	0.042	< 13.1	< 13.1	< 13.1	< 13.1	< 13.1
Sr, mg/L	109	< 0.106	< 0.106	0.110	0.42	241
Zn, mg/L	546	< 5.92	< 5.92	< 5.92	< 5.92	1890
Zr, mg/L	21.7	< 0.707	< 0.707	< 0.707	< 0.707	77.2

The mass remaining in the vessel of 468 g (325 mL) at the test conclusion was calculated based on condensate collected, thus neglecting non-condensable compounds. Based on changes in Al and Fe concentrations (non-volatile species) in the evaporator vessel during evaporation the ending material was calculated to weigh 439 g (305 mL) and 464 g (322 mL), respectively. Based on the measured density of the solution, this mass loss corresponds to a 78-80% reduction in volume. During dewatering operations, some cesium was seen in the carryover. Cs, Sr and Sm were carried over during azeotropic boiling. Sr and Cs are extremely soluble and mobile, therefore some carryover is expected. Similar carryover of Na likely occurred but could not be observed due to the much higher detection limit for this metal. The carryover of Sm independently of other more concentrated metals is doubtful and it is likely that additional analysis would indicate sample or analytical error.

Results indicate that Ce, La, Mg, and Sr may have precipitated from solution during evaporation (concentrations of other species increased during evaporation by a factor of ~4x versus the concentrations of these metals which increased by ≤ 3x). White crystalline solids were observed in the vessel the following morning. Prior to restart, the liquid level was visually observed to be below the heated area of the rods, thus 192 grams of DI water was added to the vessel such that when the mixer was turned on the liquid covered the heating rods. Thus the starting concentration of the constituents was calculated from

⁸ Total IX2 simulant added during evaporation as two portions with masses of 1212 and 606 g.

the sample results of the evaporator bottom seen in Table 4-22 accounting for the added water. The concentrated raffinate was heated to 90 °C, while stirring at 500 RPM, before concentrated (88 wt%) formic acid was pumped into the vessel subsurface at a formic to nitric acid molar ratio of 1.06 (total mass of 268.7 g of concentrated formic acid added). The average formic acid addition rate was 2.3 mL/min. The chiller was set to 15 °C and 86.7 grams of condensate was collected during formic acid addition in two batches (batch #1: 42.4 g; batch #2: 44.3 g). The vessel was allowed to react at 90 °C for four hours, before sampling. The results of the denitrated solution analysis can be seen in Table 4-23. The ending theoretical simulant mass was determined based on the concentrations of Al and Fe (i.e. 567 g and 554 g, respectively)¹⁰. The equivalent, calculated final vessel volume of 510 mL corresponds to a 28% reduction in volume relative to the sum of volumes for the diluted evaporator bottom and the formic acid. The nitrate concentration in the evaporator bottom was reduced to less than 1 M as a result of formic acid addition, and the total free acid was low, 0.10 M, which represents ideal conditions for oxalate precipitation. The denitrated bottoms are concentrated, but the mass balance indicates that Ce, La, Mg, Sr, Zn, and Pr have gone back into solution. Only Zr was a bit low. High nitrate anion and free acid concentrations were observed for the 1st condensate, presumably due to absorption of NO_x gases into the condensate.

Table 4-23. Large Scale IX Raffinate Formic Acid Denitration Results

	Initial Diluted Evaporator Bottoms⁹	1st Condensate	2nd Condensate	Denitrated Evaporator Bottoms
Simulant or Condensate Mass, g	619	42.4	42.3	561 ¹⁰
Density, g/mL	1.27	1.25	1.06	1.10
Free Acid, M	-	8.40	1.18	0.10
Formate, M	< 0.022	< 0.022	< 0.022	1.779
Nitrite, M	< 0.022	0.046	< 0.022	< 0.022
Nitrate, M	9.040	8.628	1.903	0.923
Oxalate, M	< 0.011	< 0.011	< 0.011	< 0.011
Al, mg/L	11,321	< 48.2	< 48.2	10700
Ce, mg/L	230	< 0.401	< 0.401	1,190
Cs, mg/L	567	0.011	0.067	560
Fe, mg/L	2,720	< 20.4	< 20.4	2,630
La, mg/L	99.1	< 0.902	< 0.902	515
Mg, mg/L	1,790	< 2.17	< 2.17	3,020
Mo, mg/L	217	< 8.62	< 8.62	189
Na, mg/L	458	< 5.08	< 5.08	434
Sm, mg/L	271	0.023	0.01	318
Sn, mg/L	13.1	< 13.1	< 13.1	13.1
Sr, mg/L	148	< 0.106	< 0.106	280
Zn, mg/L	1,163	< 5.92	< 5.92	1,460
Zr, mg/L	47.5	< 0.707	< 0.707	28.0

⁹ Numbers determined theoretically based on the dilution of the Final Concentrated Raffinate Simulant Results (see Table 4-22).

¹⁰ Determined theoretically. One mass estimate for the denitrated bottoms was determined using the concentration difference in Al between the diluted bottoms and the denitrated bottoms (result was 567 g). A second estimate was determined using the concentration difference in Fe between the diluted bottoms and the denitrated bottoms (result was 554 g). These two numbers were then averaged together (561 g).

The nitrate ion concentration from the large-scale test is consistent with results from the small-scale test (Figure 4-18). The residual formate ion concentration in the large-scale test is significantly lower than the small-scale test. This may be a result of metering the formate into the simulant subsurface.

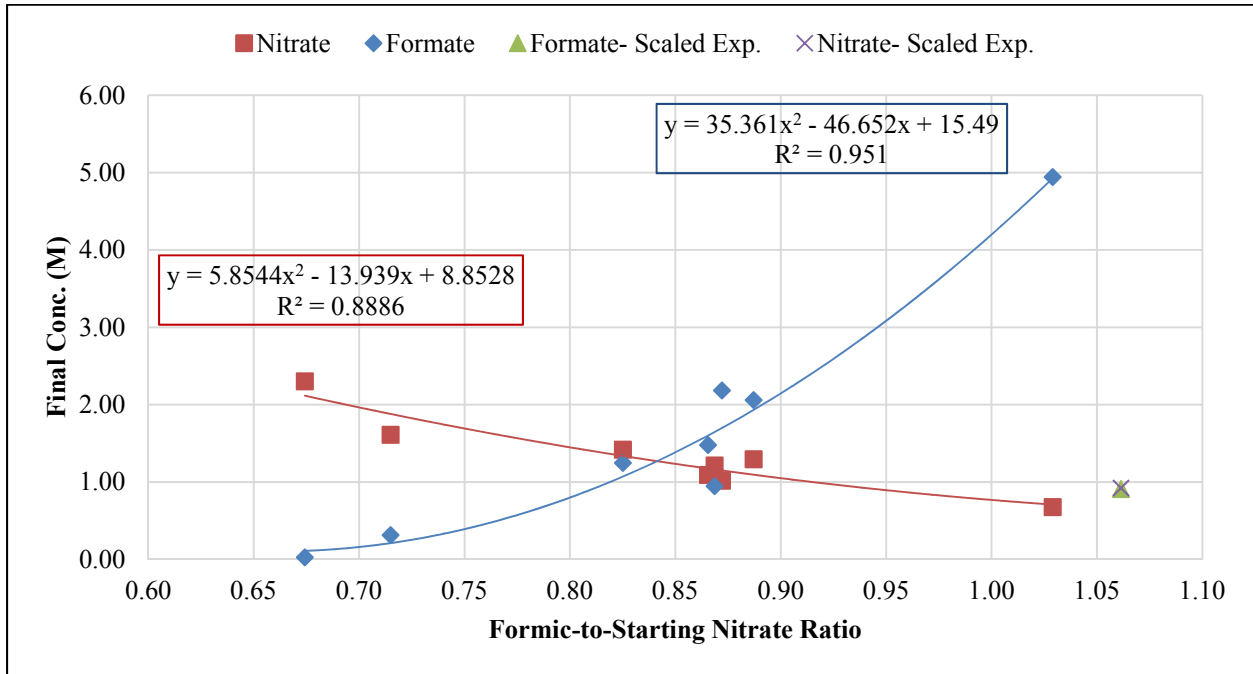


Figure 4-18. Nitrate and Formate Ion Concentrations during Large- and Small-Scale Denitration Experiments

During and after formic acid addition, the off gas was periodically sampled using 1 L Tedlar[®] bags. The off gas was sent through a RAMAN spectrometer to determine the off gas constituents. After ~13 minutes the reaction reached the inception point, after this time gases could be observed coming out of the vessel, and a foam layer formed above the solution. The appearance of the gas became more brown with processing time, indicating increasing amounts of NO_x gas was released as the reaction proceeded. Towards the end of the formic acid addition (~75 minutes) the gas became clearer. The off gas analysis results can be seen in Figure 4-19.

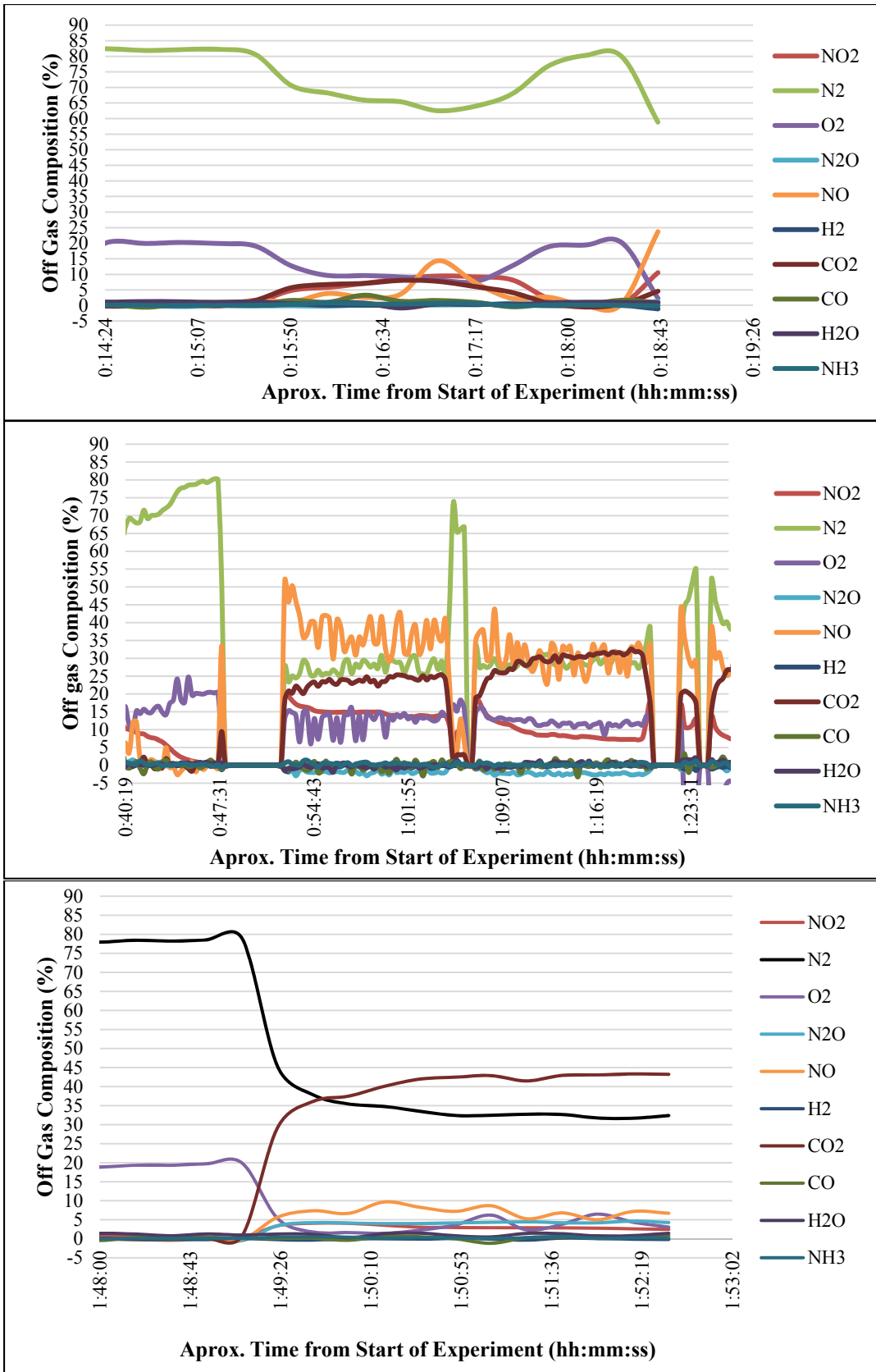


Figure 4-19. Off Gas Data for Large-Scale IX Raffinate Formic Acid Denitration Test

Off gas analysis results did not indicate the presence of hydrogen, carbon monoxide, or ammonia. Water vapor was observed in the off gas more towards the beginning of the experiment. NO and CO₂ were the primary off gas species observed with CO₂ gas becoming more prevalent towards the end of the addition indicating formic acid decomposition. It was also seen that the NO₂ concentration in the off gas decreased with time. This was expected as the nitrate ion concentration in solution dropped below ~ 4M (see Equation 2). After formic acid addition was complete, some N₂O was seen in the off gas, which is an indicator that the nitrate concentration was below ~1M (see Equation 1).

The kinetic shifts, described in Equation 1 through Equation 4, which are relatively easily detected by off gas analysis, are consistent with the nitrate destruction curves seen in Figure 4-4. The high nitrate concentration decreases relatively quickly and then slows over time, while the ingrowth of CO₂ occurs.

Following denitration, the vessel was cooled to room temperature and left overnight. The next morning the vessel was heated to 60 °C, while being stirred at 500 RPM. Then 164 mL of 0.83 M oxalic acid (0.14 moles) was added subsurface at 8.0 mL/min. The resulting 0.202 M of oxalic acid solution in the vessel was 0.10 M in excess of the stoichiometric amount of oxalate required (0.10 M). Upon completing the oxalic acid addition, the temperature was decreased to 45 °C and the system was allowed to digest for two hours.

IC anion results for the filtered oxalate precipitate slurry indicate little ongoing reaction (stable concentrations) between the nitrate and formate (Table 4-24). The free acid content was low, indicating that the target conditions were achieved for oxalate precipitation.

Table 4-24. Large-Scale IX Raffinate Oxalate Precipitation Slurry Analysis Results

	<u>Starting Condition</u>	<u>Expected Final Condition</u>	<u>Final Condition</u>
Volume, mL	510	674	-
Nitrate, M	0.923	0.698	0.731
Formate, M	1.78	1.35	1.41
Free Acid, M	0.10	-	0.10
Oxalate, M)	-	0.202	0.155

Good DFs were observed for Ce and Sm, with negligible removal of unwanted constituents. Oxalate precipitation also removed 80% of the La from solution, one of the more difficult metals to selectively precipitate (see Table 4-25). The measured concentrations of constituents in the feed to the oxalic acid precipitation step were diluted by the oxalic acid reagent and the corrected concentrations for each metal are denoted as ‘Calculated Final Concentration’ in Table 4-25. These corrected values were compared to the measured metal concentrations following oxalic acid addition and used to calculate DFs for each metal.

Table 4-25. Large-Scale IX Raffinate Metal Oxalate Slurry Filtrate Analysis Results

<u>Metal</u>	<u>Initial Conc. Before Oxalic Acid Addition, mg/L</u>	<u>Calculated Final Conc. After Oxalic Acid Addition, mg/L (assuming no precipitation)</u>	<u>Measured Final Conc. After Oxalic Acid Addition, mg/L</u>	<u>Percent of Calculated Conc. Observed in Solution, %</u>	<u>Decontamination Factor</u>
Al	10,700	8,092	7,770	96.0%	1.04
Ce	1,190	900	72.9	8.1%	12.3
Cr	20.4	15.427	15.3	99.2%	1.01
Cs	560	424	410	96.8%	1.03
Fe	2,630	1,989	1,890	95.0%	1.05
La	515	389	81.7	21.0%	4.77
Mg	3,020	2,284	2,200	96.3%	1.04
Mo	189	143	128	89.6%	1.12
Na	434	328	308	93.8%	1.07
Sm	318.	240	0.8	0.3%	289.0
Sn	<13.1	9.907	<13.1	132%	0.76
Sr	280	212	205	96.8%	1.03
Zn	1,460	1,104	1,060	96.0%	1.04
Zr	28.0	21.2	22.000	104%	0.96

The temperature was lowered to 35 °C and the oxalate slurry was transferred out of the vessel through the bottom vessel port, while stirring at 500 RPM, through a 0.1µm CN disk that was 90 mm in diameter. The filtrate was weighed and sampled (see Table 4-25). The wet cake was allowed to dry overnight, weighed, and then calcined. The same calcination heating profile was used as that used for the previous small-scale experiment, thus the sample was held at 1000 °C for two hours.

As discussed earlier, the mass loss due to non-condensable gasses was not determined. The mass remaining in the vessel was estimated using the ratio of Al and Fe after denitration. Further, there is some holdup of solids in the vessels after draining through the filter. Mass data collected during the large-scale calcination are provided in Table 4-26. During calcination, ~56% mass loss was observed from the sample (wet metal oxalate precipitate + filter).

Table 4-26. Large-Scale Oxalate Precipitation and Calcination Mass Data

<u>Calculated Denitrated Filtrate + Oxalic Acid, g</u>	<u>Measured Denitrated Filtrate + Oxalic Acid, g</u>	<u>Variance in Mass, g</u>	<u>Wet Precipitate + Filter Paper, g</u>	<u>Calcined Weight, g</u>
731	625	106	7.498	3.316

TGA-MS was performed on the calcined metal oxide material. During TGA-MS analysis the sample was heated to 1000 °C over a period of ~70 minutes. The TGA-MS results, seen in Figure 4-20 and Figure 4-21, indicated that 1.44 wt% was lost during heating, with the majority of mass loss occurring at temperatures greater than 450 °C. However, the mass spectrometer results did not detect a significant amount of material in the off gas. The main component detected was CO₂, with a small amount of NO₂.

These components do not account for the sample weight loss observed. Mass loss under these conditions could be associated with the decomposition or sublimation of various cesium or sodium metal oxides. The observed mass loss exceeds the specification limit of 0.5 wt. % for the shipment of the oxide product. Additional research would be needed to determine the source of the mass loss or optimize washing or calcination conditions for the oxalate product to decrease mass losses for the oxide product to below the specified value.

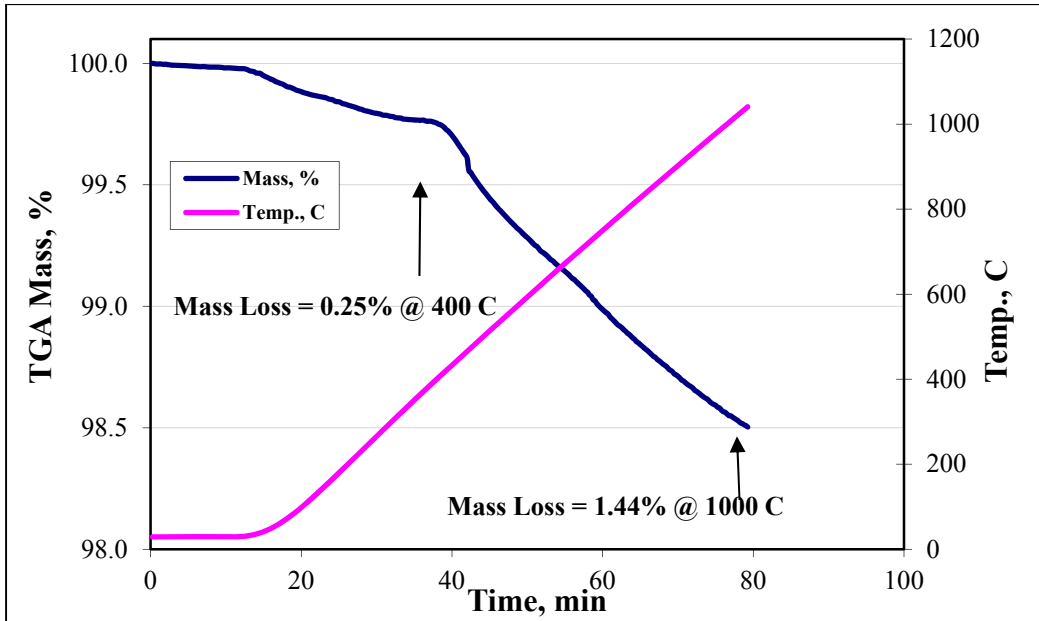


Figure 4-20. TGA Plot of Calcined Large-Scale Metal Oxide Product

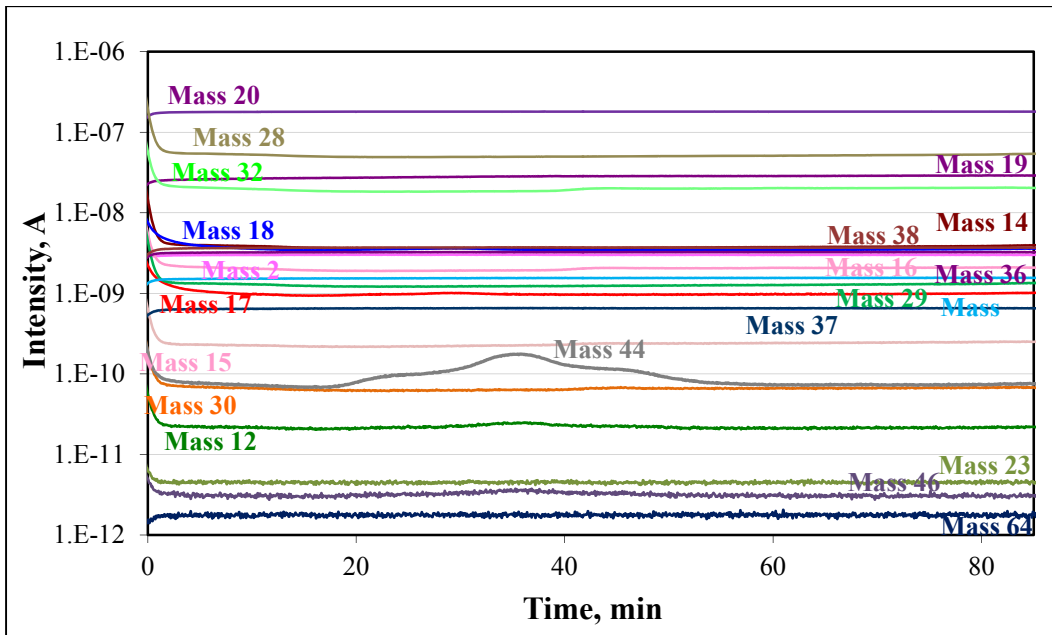


Figure 4-21. MS Plot of Calcined Large-Scale Metal Oxide Product during TGA Analysis

The calcined material was dissolved by peroxide fusion and the digestion solution was analyzed. Analysis results are provided in Table 4-27. As expected, the dominant metals present in the calcined oxide solids are the rare earth elements Ce, Eu, Gd, La, Nd, Pr, and Sm.

Table 4-27. Elemental Composition of the Metal Oxide Product from the Large-Scale Test

<u>Component</u>	<u>Elemental Conc., µg/g</u>	<u>Oxide Conc., wt%</u>
Al	< 346	< 0.07%
Ce	135,000	15.81%
Cs	164	0.02%
Eu	22,200	2.57%
Fe	949	0.14%
Gd	81,500	9.39%
La	37,200	4.36%%
Mg	< 206	< 0.03%
Mo	2520	0.38%
Nd	164,000	19.13%
Pd	5600	0.64%
Pr	332,000	38.85%
Re	26.9	0.00%
Ru	6.34	0.00%
Sm	31,700	3.68%
Sn	165	0.02%
Sr	176	0.02%
Zn	613	0.08%
Carbon	132	0.05%
SUM	-	95.24%

A mass balance was attempted across the proposed flowsheet. Results are provided in Table 4-28. Less than detectable values were assumed to be zero for conservatism. The mass balance indicates that if the missing Na and Cs (see Total Loss in Table 4-28) was combined with the detected Na and Cs in the calcined oxide product (see Calcine Oxide Solid in Table 4-28) this would result in a total calcined weight percent of 1.51% and 1.78%, respectively for Na and Cs, which does not aid in determining the source of the mass loss (1.44%, see Figure 4-20) during TGA. Very high losses (>35%) were observed for Ce, Pd, Re, and Zr. Significant losses (20-35%) were also observed for Eu, Gd, La, Mo, Nd, Pr, and Sm. The oxalate slurry filtrate was not fully analyzed and it is likely to contain some additional metals. There may also be Zr in the calcined product, but the concentration of this metal in the original solution could not be determined because peroxide fusion was conducted in a Zr crucible.

Table 4-28. Overall Mass Balance Results for the Overall Large-Scale Waste Treatment Process

<u>Metal</u>	<u>Initial Mass, mg</u>	<u>Mass Removed with Condensate, mg</u>	<u>Mass Removed by Sampling, mg</u>	<u>Mass after Formic Acid Denitration, mg</u>	<u>Mass in Metal Oxalate Slurry Filtrate</u>	<u>Calcined Oxide Solid, mg</u>	<u>Total Loss</u>
Al	5613	-	858	5455	4539	0	3.9%
Ce	864	0.02	47.5	607	42.6	438	38.9%
Cs	339	0.16	43.7	286	240	0.5	16.3%
Eu	132	0.00	17.5	123	-	73.6	30.8%
Fe	1424	0.24	208	1341	1104	3.1	7.6%
Gd	531	0.00	69.9	496	-	270	36.0%
La	268	0.01	20.5	263	48	123	28.6%
Mg	1629	0.03	177	1540	1285	0	10.2%
Mo	127	0.10	16.0	96	75	8.36	21.6%
Na	252	0.06	34.7	221	180	0.00	14.7%
Nd	951	0.00	137	889	-	544	28.4%
Pd	47.4	0.00	7.2	46.0	-	18.6	45.5%
Pr	1938	0.00	148	1810	-	1101	35.5%
Re	63.9	0.00	9.8	62.1	-	0.1	84.6%
Sm	190	0.01	22.5	162	-	0.11	32.7%
Sr	165	0.04	15.6	143	120	0.58	17.6%
Zn	824	-	99.2	744	619	2.03	12.5%
Zr	33	-	3.1	14.3	12.9	-	51.5%

The tap density of the metal oxide product from the large-scale calcination experiment, determined per L29 ITS-0187, was 1.034 g/mL. The final oxide mass was 3.316 g, using the tap density this equates to an ending volume of 3.2 mL. Given the starting IX raffinate simulant volume, 1510 mL, the total volume reduction of the waste treatment process was 99.79%.

5.0 Conclusions

Research presented in this report indicates that evaporation of the IX raffinate to reduce the volume, followed by formic acid denitration, would allow rare earth and (presumably) transuranic metals to be precipitated by an oxalic acid strike, which can subsequently be calcined to form an oxide product. During evaporation, water- and nitric-acid rich streams can be removed to significantly reduce the volume of the feed. These cuts can likely be recycled within the flowsheet. A small amount of Cs was observed in the water-rich cut. A higher amount of Cs and likely some Na, along with Sr and some Sm were seen in the nitric acid cut. The Sm result was suspect. Given the solubility and known mobility of Na carryover was likely present below the detection limit.

Denitration with formic acid was required to reduce the nitric acid concentration to < 1 M NO₃ to selectively precipitate rare earths and transuranic metals. The study indicated that 0.90 moles of formic acid per mole of nitric acid was the minimum ratio needed to sufficiently destroy the nitrate ion. The residual nitrate ion concentration had greater impact on the selective precipitation of the rare earth metals tested (La, Ce, Pr, Nd, Sm, Eu, and Gd) than the residual formic acid concentration. As the ratio of the moles of formic to nitric acid is increased much above 1, the amount of residual formate ion increases, without a significant decrease in the nitrate ion concentration. It is recommended to target a formate-to-nitrate ratio between 0.90 and 1.06. During formic acid treatment, a significant amount of NO_x was

generated, but the off gas did not contain measurable hydrogen, carbon monoxide, or ammonia. Formic acid addition causes foaming; therefore, it is necessary to control the reagent addition speed. At the 1.5 L large-scale experiment, the maximum formic acid addition rate used was 2.31 ml/min. Formic acid treatment to promote denitration is the rate limiting step of the unit operations proposed.

Oxalic acid should be added in a stoichiometric excess of approximately 0.2 M or greater. The nitrate ion concentration significantly impacts the selective precipitation of the rare earth elements studied. The difficulty of precipitation appears to be in the order $\text{Eu} < \text{Sm} < \text{Gd} < \text{Nd} < \text{Pr} < \text{Ru} < \text{Ce} < \text{La}$. Eu DF was ~ 1400 , whereas the La DF was ~ 6 . Cm is expected to behave like Sm, which had a DF of ~ 290 . Increasing the addition rate appears to promote formation of smaller particles. Initial testing that used isopropanol in oxalic acid indicates that increased DFs can be achieved by changing the dielectric constant of the solution. It may be worth performing additional testing to investigate the use of isopropanol in oxalic acid to increase recovery of the desired metals.

Filtration of the metal oxalate precipitate was easily achieved and was performed with polycarbonate or polypropylene filters. With time, additional solids form in the filtrate that are believed to be aluminum or sodium oxalate salts. Therefore, it is recommended to not delay filtering.

TGA-MS results indicate that the calcined product is dry, but loss of ~ 1.6 wt% was observed that is likely associated with a volatile metal oxide. The volatilization of Cs or Na-containing species could be the source of the mass loss. Additional R&D is needed to confirm that increased calcination time or calcination under forced air conditions would be sufficient to meet packaging targets (mass loss < 0.5 wt%).

6.0 References

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Appendix A. Additional Data

Table A-1. N1 Evaporation Data

<u>Time,</u> <u>min</u>	<u>Bottom</u> <u>Temperature, °C</u>	<u>Chiller</u> <u>Temperature, °C</u>	<u>Condensate Volume,</u> <u>mL</u>
0.0	31.6	19.9	-
15.0	108.1	14.4	-
18.7	119.9	14.9	-
20.3	120.5	15.0	-
24.5	120.5	15.2	-
30.0	121.2	15.0	-
31.5	121.2	15.0	0
38.0	121.5	15.0	25
49.8	122	15.0	50
72.3		15.0	75
73.7		15.0	104
89.0		15.0	126
89.3		15.0	126
109.2		15.0	151
111.2		15.0	184
135.0		15.0	209
163.0		15.0	234
164.5		15.0	266
190.8		15.0	291
196.3			330
196.6		13.0	
215.5			
220.5			
222.3			
222.9			
223.0		13.0	

Table A-2. N2 Evaporation Data

<u>Time,</u> <u>min</u>	<u>Bottom</u> <u>Temperature, °C</u>	<u>Chiller</u> <u>Temperature, °C</u>	<u>Condensate Volume,</u> <u>mL</u>
0.0	23.0	19.0	-
12.2	98.5	13.8	-
19.7	118.5	12.7	-
30.0	138.7	13.1	-
34.0	161.5	13.0	0
72.0	261.5	13.0	50
78.0			
78.8			
101.8			70
101.4	461.2	13.0	
114.8			
116.0			122
125.5	247.9		142
154.8	83.4	13.0	

Table A-3. IX1 Evaporation Data

<u>Time,</u> <u>min</u>	<u>Bottom</u> <u>Temperature, °C</u>	<u>Chiller</u> <u>Temperature, °C</u>	<u>Condensate</u> <u>Volume,</u> <u>mL</u>
1.0	33.9	14.5	-
10.0	58.6	15.1	-
14.0	70.1	15.0	-
23.0	93.7	15.0	-
25.8	100.3	15.0	-
33.0	111.8	15.0	-
38.0	112.6	15.0	-
49.0	113.6	15.0	0
53.0	113.7	15.0	
62.0	114.2	15.0	
72.0	114.6	15.0	
85.0	115.7	15.0	
95.0	116.5	15.0	
98.5	116.8	15.0	25
102.0	116.8	15.0	50
114.5	118.4	15.0	
123.0	118.4	15.0	
124.0	118.4	15.0	
134.0	120.0	15.0	110
135.0	120.1	15.0	
142.8	120.7	15.0	
150.0	120.6	15.0	162
152.0	120.7	15.0	
154.0	120.7	15.0	192
155.0	120.6	15.0	

Table A-4. IX2 Evaporation Data

<u>Time,</u> <u>min</u>	<u>Bottom</u> <u>Temperature, °C</u>	<u>Chiller</u> <u>Temperature, °C</u>	<u>Condensate</u> <u>Volume,</u> <u>mL</u>
0.0	17.0	19.9	-
15.0	43.2	18.8	-
73.0	113.9	14.5	-
76.0	114.0	15.0	0
101.0	115.8	15.0	25
102.0	115.8	15.0	
116.0	117.0	15.0	
122.0	117.7	15.0	
129.5	118.2	15.0	
141.5	119.1	15.0	
142.0	119.7	15.0	
142.0	120.0	15.0	92
149.5	120.0	15.0	
161.5	120.7	15.0	
170.7	121.0	15.0	
181.0	121.1	15.0	
191.0	121.1	15.0	
201.0	121.1	15.0	
210.0	121.1	13.0	
215.0	121.1	13.0	153

Table A-5. IX2 Evaporation Data

	<u>Calc.</u> <u>Final</u> <u>Volume,</u> <u>mL</u>	<u>Al,</u> <u>mg/L</u>	<u>Fe,</u> <u>mg/L</u>	<u>La,</u> <u>mg/L</u>	<u>Mg,</u> <u>mg/L</u>	<u>Na,</u> <u>mg/L</u>	<u>Sm,</u> <u>mg/L</u>
Starting Simulant	90.0	14700	3200	3670	4330	3630	1744
Test 1	134.3	10300	2280	1270	3080	2400	-
Test 2	133.8	10400	2290	1330	3100	2320	-
Test 3	139.3	9860	2150	1000	2890	2230	-
Test 4	139.6	9860	2170	1030	2950	2170	-
Test 5	127.2	10200	2240	1220	3020	2410	-
Test 6	127.3	10500	2310	1340	3130	2320	-
Test 7	116.8	11600	2550	2140	3450	2560	-
Test 7I	126.5	10700	2360	1350	3180	2370	-
Test 8	117.0	11600	2540	2130	3440	2570	-
Test 8I	126.6	10700	2340	1350	3160	2350	-
Test 9	116.8	11500	2510	1780	3390	2490	-
Test 10	124.4	10600	2320	1280	3140	2320	-
Test 11	139.1	8490	1880	1200	2870	2080	83.7
Test 12	137.4	8710	1930	1330	2870	2140	95.8
Test 13	133.3	10400	2260	1150	3060	2280	-
Test 14	133.1	10300	2260	1160	3060	2310	-
Test 15	133.5	10100	2210	1220	3000	2230	-
Test 16	133.4	10100	2210	1220	2980	2560	-
Test 17	138.2	8700	2060	1030	2740	1880	51.9
Test 18	140.6	8560	2050	572	2720	1890	-
Test 19	135.7	9710	2330	1170	3100	2130	-
Test 20	135.8	9830	2340	1150	3120	2180	179

Table A-6. Simple Simulant Oxalate Results

<u>Test #</u>	<u>Al DF</u>		<u>Fe DF</u>		<u>Mg Df</u>		<u>La DF</u>		<u>Na DF</u>	
1	0.96	0.95	0.94	0.94	0.94	0.91	1.94	1.90	1.01	1.03
2	0.95		0.94		0.94		1.86		1.05	
3	0.96	0.96	0.96	0.96	0.97	0.96	2.37	2.33	1.05	1.07
4	0.96		0.95		0.95		2.30		1.08	
5	1.02	1.00	1.01	1.00	1.01	1.00	2.13	2.03	1.07	1.09
6	0.99		0.98		0.98		1.94		1.11	
7	0.98	0.98	0.96	0.97	0.97	0.97	1.93	1.93	1.09	1.09
8	0.98		0.97		0.97		1.93		1.10	
9	0.99	0.99	0.98	0.99	0.98	0.99	1.59	1.83	1.12	1.13
10	1.00		1.00		1.00		2.07		1.13	
11	1.12	1.11	1.10	1.09	0.98	0.98	1.98	1.89	1.13	1.12
12	1.11		1.09		0.99		1.81		1.11	
13	0.95	0.96	0.96	0.96	0.96	0.96	2.15	2.15	1.07	1.07
14	0.97		0.96		0.96		2.14		1.06	
15	0.98	0.98	0.98	0.98	0.97	0.98	2.03	2.03	1.10	1.03
16	0.98		0.98		0.98		2.03		0.96	
17	1.10	1.10	1.01	1.01	1.03	1.02	2.32	3.21	1.26	1.24
18	1.10		1.00		1.02		4.11		1.23	
19	1.00	1.00	0.91	0.91	0.93	0.92	2.08	2.10	1.13	1.12
20	0.99		0.91		0.92		2.12		1.10	

Filter paper codes:
PC = polycarbonate
PP = polypropylene

Table A-7. Simple Simulant Mass Balance

<u>Test #</u>	<u>Total Mass Added, g</u>	<u>Filtrate Total, g</u>	<u>Missing Mass, g</u>	<u>Wet Precipitate weight + Filter Paper, g</u>	<u>Filter</u>
1	148.43	135.91	12.51	0.621	PC
2	147.48	136.97	10.51	0.681	PP
3	153.45	143.80	9.65	0.728	PP
4	153.83	145.50	8.33	0.736	PC
5	140.31	138.13	2.17	0.134	PP
6	140.78	137.78	3.00	0.036	PC
7I	129.48	123.01	6.47	-	PP
8I	129.78	-	-	-	-
7	139.44	110.25	29.20	0.736	PP
8	139.69	114.04	25.65	0.697	PC
9	128.48	124.34	4.13	0.043	PP
10	137.48	132.69	4.79	0.029	PC
11	154.35	142.36	11.99	0.328	PP
12	152.33	147.56	4.78	0.230	PC
13	145.68	111.26	34.43	0.674	PP
14	146.58	138.98	7.61	0.595	PC
15	147.37	142.12	5.25	0.637	PP
16	146.90	142.98	3.92	0.575	PC
17	167.11	153.40	13.71	0.671	PC
18	169.37	155.12	14.25	0.938	PP
19	149.34	142.62	6.72	0.519	PP
20	149.35	143.01	6.34	0.494	PC

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