Sulfate Removal Studies for

River Protection Project Part B1

UNCLASSIFIED
DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION

ADC &
Reviewing
Official: _W E Steven -L3 manager_

(Name and Title)

Date: 3/23/01

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SRS

RESPONSIBILITY · SECURITY · SAFETY

SAVANNAH RIVER SITE

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

DISCLAIMER

Sulfate Removal Studies for River Protection Project Part B1

SAVANNAH RIVER TECHNOLOGY CENTER

M. Hay, C. Coleman, N. Hassan, D. McCabe, B. King, C. Nash, H. Saito, B. Calloway, C. Crawford

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SAFETY · RESPONSIBILITY · SECURITY
SRS
SAVANNAH RIVER SITE

DOCUMENT: **WSRC-TR-2000-00489 (SRT-RPP-2000-00049)**
TITLE: **Sulfate Removal Studies for River Protection Project Part B1**
APPROVALS

_____Date:_____
M. Hay, Co-author (External Programs Group/SRTC)

_____Date:_____
C. Coleman, Co-author (Spectroscopic Research/Instrumental Analysis Group/SRTC)

_____Date:_____
N. Hassan, Co-author (Actinide Laboratory Programs Group/SRTC)

_____Date:_____
D. McCabe, Co-author (External Programs Group/SRTC)

_____Date:_____
B. King, Co-author (External Programs Group/SRTC)

_____Date:_____
C. Nash, Co-author (External Programs Group/SRTC)

_____Date:_____
H. Saito, Co-author (External Programs Group/SRTC)

_____Date:_____
B. Calloway, Co-author (Process Development Group/SRTC)

_____Date:_____
C. Crawford, Co-author (Process Development Group/SRTC)

_____Date:_____
RPP Pretreatment or Vitrification Manager

_____Date:_____
M. Crowder, Actinide Laboratory Programs, Technical Reviewer

Contents

1.0   Executive Summary

The report documents the initial test results of a sulfate removal resin and the investigation into alternative methods of sulfate removal from LAW waste streams. The work scope was reqested through test specification TSP-W375-99-00012, "Test Specification for Evaluting Sulfate Removal from LAW Solutions" and test specification TSP-W375-99-00016, "Test Specification for Separating Sulfate from Pretreated AN-107, AZ-102, and AN-102 Solutions by Precipitation" (see references 4 and 5 of section 2.0).

Initial test results using SuperLig® 655 ion exchange resin with pretreated Hanford supernate (Tank 241-AN-103) and Envelope B (Tank 241-AZ-101) simulant indicated the resin was ineffective at removing sulfate. The data indicated chromate interference and resin degradation in caustic salt solutions were responsible for the poor performance of the resin.

Evaporation tests and precipitations with calcium, strontium, and barium salts as well as organic and organometallic precipitants indicated all of the methods suffer from problems with selectivity. Precipitation with barium can be used to remove the required amount of sulfate from all of the waste envelopes. However, large increases in liquid waste volume and the generation of large quantities of secondary waste solids make the process impractical for large scale applications. In addition the solids produced from the barium precipitations would require handling and disposal as hazardous and possibly TRU waste.

Low temperature crystallization was found to lower sulfate levels in treated Envelope B simulants where sulfate levels were high, but not to sufficient levels necessary to meet LAW melter specifications.

In larger scale experiments an Envelope B simulant and a active sample of 241-AN-102 (Envelope C) were successfully decontaminated of sulfate and evaporated. However, as in the smaller scale experiments, problems with selectivity and large increases in waste volume were observed. A glass formulation was developed for the vitrification of the 241-AN-102 sample; however, the concentrated sample was not vitrified due to cancelation of the sulfate pretreatment program.

2.0   Introduction and Background

The Department of Energy, Office of River Protection (DOE/ORP) is utilizing subcontractors to design, construct, and operate facilities to immobilize radioactive waste stored in underground tanks at the Hanford site near Richland, Washington.[1,2] The program is called the River Protection Project Waste Treatment Plant (RPP-WTP). The current phase of this project is referred to as Part B-1 and includes activities for verification of technology and design of waste treatment facilities.

The RPP-WTP will treat High Level Waste and Low Activity Waste (LAW) from underground storage tanks and incorporate the treated waste in glass. The LAW feed solutions can contain up to 0.07 moles of sulfate per mole of sodium. The high concentrations of sulfate present problems for the LAW vitrification. Preliminary testing of the LAW vitrification system indicated that a separate molten sulfur layer will form in the melter at the maximum sulfate to sodium mole ratio in the LAW solutions.[3] A molten sulfur layer in the LAW melter can lead to accelerated corrosion of the melter and unacceptable operating conditions (e.g., steam explosion) and a vitrified waste form that does not meet the waste acceptance criteria. The pretreatment flowsheet for the Hanford River Protection Project requires sulfate removal from the LAW solutions. Table 2.1 shows the sulfate to sodium molar ratio for waste and the maximum ratio allowable in the glass for each envelope.

Table 2.1. Sulfate to Sodium Molar Ratios in LAW Waste Envelopes and Maximum Ratios Allowable in the Glass.

Waste Envelope	Representative Tank	SO_4:Na Molar Ratio in Waste	Max. SO_4:Na Molar Ratio in Glass
Env. A	241-AN-105	0.01	3.87E-03
Env. B	241-AZ-101	0.07	9.68E-03
Env. C	241-AN-102	0.02	4.55E-03

As a result of these concerns BNFL Inc., the intial contractor for the RPP, pursued the development of a sulfate removal resin. However, initial testing of the resin with simpified waste stream simulants indicated marginal performance with respect to the removal of sulfate. BNFL Inc. tasked SRTC with investigating alternative methods for removing sulfate from the waste.[4, 5]

A literature search and brainstorming session generated the following list of potential sulfate removal methodologies:

- Ion Exchange - other resins
- Evaporation - both with and without precipitating agents
- Precipitation - inorganic and organic precipitating agents
- Freeze Crystallization

Alternative resins or ion exchangers identified required acid side processing and therefore, were not pursued. This report documents the initial testing of the sulfate removal resin and the results of the investigation of other sulfate removal options.

2.1   References

1. TWRS Privatization, Contract No. DE-AC27-96RL13308, Mod. No. A013, Section C: Statement of Work, 1998. (See http://www.hanford.gov/doe/contracts/de-ac06-96rl13308/sectionc-1.html)

2. Technical and Development Support to TWRS Design, K. A. Johnson and M. E. Johnson, K0104_077_PRC, December 1997.

3. K. S. Matlack et al., Final Report – Results of Melter Testing Using TWRS LAW Envelope B Simulants, 1998010122 Rev. 0, October 24, 1997, Vitreous States Laboratory, The Catholic University of America, Washington, D.C.

4. M. E. Johnson, River Protection Project Test Specification for Evaluating Sulfate Separation from LAW Solutions, TSP-W375-99-00012, Rev. 0, September 10, 1999.

5. M. E. Johnson, River Protection Project Test Specification for Separating Sulfate from Pretreated AN-107, AZ-102, and AN-102 Solutions by Precipitation, TSP-W375-99-00016, Rev. 2, January 4, 2000.

3.0   Ion Exchange

3.1   Introduction

The sulfate ion exchange process utilized SuperLig® 655 resin, which was developed by IBC Advanced Technologies for this specific application.

The objectives of the sulfate ion exchange tests were as follows:

1)   Determine the batch distribution coefficients (K_d values) and percent removal for sulfate ion with SuperLig® 655 resin using pretreated supernate from Hanford Envelope A Tank AN-103 and Envelope B Tank 241-AZ-101 simulant.
2)   Demonstrate sulfate ion exchange column loading and elution profiles.

3.2   Experimental

Pretreated Hanford Tank Supernate of Envelope A (AN-103) and an Envelope B simulant (AZ-101) were used for the determination of batch distribution coefficients and column breakthrough and elution efficiency tests. The as-received AN-103 sample was diluted to near 5.9 M Na^+, filtered to remove entrained solids, and subjected to ion exchange treatments for the removal of cesium and technetium. The sulfate concentration in the pretreated sample was increased to 0.053 M by the addition of Na_2SO_4 prior to sulfate ion exchange testing. Table 3.1 shows the characterization data for the pretreated AN-103 sample. The "as prepared" AZ-101 simulant composition is provided in Table 3.2. Analysis results for the simulant are provided in Attachment 1 of Appendix 1. Although the target AZ-101 simulant composition contained 0.18 M sulfate, analytical results by ICP-ES and ion chromatography indicated that the sulfate concentration was approximately 0.09 M. The measured chromate concentration was also lower than expected based on ICP-ES analysis (5.88E-03 M, 59% of the target concentration). ACS certified reagents from Fisher Scientific, Inc were used for the preparation of simulant and resin pretreatment, wash, and eluent solutions. The ion exchange resin used in this study was SuperLig® 655 (batch # 990808DHC-8-030). IBC Advanced Technologies, American Fork, Utah, supplied the resin in 1.0 M $NaNO_3$ solution.

Table 3.1. Characterization of pretreated Hanford supernate (Tank 241-AN-103)

Constituent	Molarity
Na^+	4.79
Al	0.63
Cr	1.34E-03
P	9.59E-03
Si	1.62E+02
NO_2^-	8.83E-01
NO_3^-	9.09E-01
Cl^- by IC	7.37E-02
F^- by IC	4.53E-03
SO_4^{-2}	5.52E-02
PO_4^{-3}	4.94E-03
TIC (mg/L)	2084
TOC (mg/L)	1644
Radionuclides	
Cs-137 uCi/ml	1.15
Tc-99 by ICP-MS (mg/L)	0.089

Table 3.2. Envelope B (Tank 241-AZ-101) Simulant Composition (As-prepared)

Constituent	As-prepared (M)
$NaNO_3$	1.08
KNO_3	0.12
$NaNO_2$	1.41
$CsNO_3$	2.87E-04
$ZrO(NO_3)_2$	3.61E-05
NH_4NO_3	1.84E-02
NaOH	0.93
$Al(OH)_3$	0.40
NaCl	0.01
NaF	0.10
Na_2CO_3	0.38
Na_2SO_4	0.18
Na_3PO_4	1.58E-02
$NaCrO_4$	1.44E-02
Total Na^+	4.71
Total NO_3^-	1.22
Free OH^-	0.54

The equipment used for batch contact tests consisted of 30 mL polyethylene bottles, a Mix-Max®
orbital shaker, nylon filter units, plastic filter holders, and analytical balances accurate to ± 0.001 g.

The ion exchange column design was the same as that reported in previous documents.[1,2] The ion
exchange columns were made of medium-wall Pyrex glass tubes. The column used with pretreated
Hanford supernate had an inside diameter of 1.1 cm. The column used with Envelope B simulant had an
inside diameter of 2.69 cm. Three-way Teflon® stopcocks were attached to the bottoms of the columns
and two 2-way Teflon® stopcocks were attached on opposite sides of the column heads to serve as
inlet ports. The column head also contained a pressure gauge, a pressure relief valve, and a fill reservoir
that also served as a vent. Stainless steel wire screens (200 mesh) were inserted into the bottoms of the
columns to support the ion exchange resin. Decals were affixed to the outer walls of the columns with 1
mm graduations to measure the resin bed height and liquid level. A plastic coating was applied to the
outside walls of the columns to contain shattered glass in case of a rupture. Colder Products Company
polypropylene quick-disconnect couplings were used to connect low-density polyethylene tubing
(11/64" ID) to the columns. Solutions were passed through the columns using Fluid Metering
Incorporated QG150 positive displacement pumps with ¼" and $^3/_8$" piston sizes.

The ion exchange column and batch contact experiments with pretreated Hanford supernate were
performed in a shielded cell, allowing remote handling of the materials. The batch contact and column
tests with Envelope B simulant were performed in a chemical hood.

The batch contact experiments were conducted in duplicate using the same batch of "as received" resin.
In each batch contact test, the SuperLig® 655 resin/1 M $NaNO_3$ slurry was transferred into a small,
calibrated graduated cylinder to give a total settled resin volume near 0.6 mL. Excess liquid was
removed from above the resin using a pipette. Special care was taken to avoid drying the resin by
removing too much liquid or inadvertently removing resin when pipetting liquid from the cylinder. A
known volume of salt solution (~5 mL, calculated from the solution mass and known density) was
added to the cylinder and the slurry was transferred to a polyethylene bottle. Careful techniques were
used to ensure that all of the resin was transferred to the bottle. The bottles containing the solution and
resin were then placed on the orbital shaker and gently shaken for 24 ±1 hours at ambient temperature
(25±1 °C). Control samples containing ~5 mL of pretreated supernate or simulant were treated in the
same way as those of duplicate test samples without the addition of the resin. The measured sulfate
concentration in control samples was used as the initial concentration for determining the K_d values and
percent removed by the resin. The ambient cell or chemical hood temperature was recorded at the
beginning and end of each test. After the contact period, the resin was separated from the sample
solution by filtration through an individual 0.45 micron nylon filter unit. A 1 mL sub-sample of the filtrate
was removed from the cell or chemical hood and analyzed by the Analytical Development Section at the
Savannah River Technology Center (SRTC). The sulfate concentration was determined before and after
contact with SuperLig® 655 resin by ion chromatography (IC).

Sulfate removal testing with pretreated Hanford supernate (Tank AN-103) and Envelope B simulant (AZ-101) was accomplished with single ion exchange columns. The resin was slurried into the columns with 1.0 M NaNO$_3$ solution. The column walls were tapped while the resin slurry was being added to ensure uniformly packed beds. The wet volume of the resin in the columns used with pretreated Hanford supernate was 5.2 ml while that used with simulant was 30.0 ml. The feed solution was pumped down flow through the columns at 3 CV/hr (CV = column volumes) . The liquid level in the columns was maintained at 1-2 cm above the resin during the loading cycle. Sub-samples were collected from the bottom of each column at 1 CV intervals. Upon completion of the sulfate loading cycle, the resin was washed with 2 CV of a 0.1 M NaOH/0.25 M NaNO$_3$ solution followed by 2 CV of 0.25 M NaNO$_3$ solution. The resin was then eluted with 0.5 M HNO$_3$. The nitric acid was pumped down flow through the columns and sub-samples of the eluate were collected at 1-2 CV intervals. Eluate samples were analyzed for sulfate content by ion chromatography.

The data reporting and data quality requirements were specified in the task specification.[3]

3.3   Results and Discussion

Batch contact experiments were performed to determine equilibrium distribution coefficients (K$_d$ values) and percent removal of sulfate. The batch contact experiments include the addition of a small quantity of ion exchange material into a small volume of the salt solution containing known quantities of sulfate ions. The concentration of sulfate in pretreated Hanford supernate and Envelope B simulant was determined by ion chromatography (IC) before and after contact with the SuperLig® 655 resin. The quantity of sulfate ions on the resin was determined by difference. Data for the batch contact tests with pretreated Hanford Envelope A supernate and Envelope B simulant are provided in Attachments 2 and 3 of Appendix 1. Note that the data are presented in units of mL/g, despite the fact that the batch distribution measurements were done using volumetric measurements. This is because the resin was not dried and weighed. Drying the resin reportedly destroys it. Hence, the vendor stated density of the as received resin (0.4 g/mL) was used to convert the Kd data into per mass unit basis.

Sulfate distribution coefficients and % removal were calculated for each experiment using the formulas shown in Eqs. 1 and 2, respectively.

$$K_d = [(C_i/C_f) - 1][V_s/V_r] \qquad (1)$$

$$\% \text{ removal} = \frac{(100)*(C_i - C_f)}{C_i} \qquad (2)$$

C_i = initial $[SO_4^{2-}]$ in feed (mg/L)
C_f = final $[SO_4^{2-}]$ after contact (mg/L)
V_s = volume of solution used (mL)
V_r = mass of "as-received" resin in 1 M $NaNO_3$ (g, calculated)

The K_d values and percent removal for SO_4^{-2}, Cr, PO_4^{-3}, Cl^- and F^- ions from pretreated Hanford supernate and Envelope B simulant are presented in Tables 3.3 and 3.4. The data show that the resin is not highly effective for SO_4^{-2} removal from salt solutions. The sulfate K_d values for pretreated Hanford supernate and Envelope B simulant were 6.5 and 6.8 mL solution/mL resin (average of duplicate samples), respectively. These K_d values correspond to 24-25 % sulfate removal. The K_d values for Cr from pretreated Hanford supernate and Envelope B simulant were higher at 16.0 and 11.3 mL solution/mL resin, respectively (corresponding to 35-45% Cr removal). These results suggest that CrO_4^- competes with SO_4^{2-} for adsorption sites on the resin.

Table 3.3. K_d values and % removal from pretreated Hanford supernate

Constituent	K_d (mL/g)	% removal
SO_4^{2-}	6.56	23.6
Cr	15.98	42.8
PO_4^{3-}	2.89	11.7
Cl^-	1.15	4.99
F^-	0.39	1.72

Table 3.4. K_d values and % removal from Envelope B simulant

Constituent	K_d (mL/g)	% removal
SO_4^{2-}	6.8	24.7
Cr	11.3	35.1
PO_4^{3-}	3.3	13.7
Cl^-	2.1	9.2
F^-	1.7	7.4

The sulfate breakthrough data for SuperLig® 655 column loading is provided in Tables 3.5 and 3.6 for pretreated Hanford supernate and Envelope B simulant, respectively. The concentration profiles (C/Co) for SO_4^{-2}, Cr, PO_4^{-3}, Cl⁻ and F⁻ are plotted in Figures 3.1 and 3.2 for the pretreated Hanford supernate and Envelope B simulant, respectively. Attachments 4 and 5 of Appendix 1 provide complete column breakthrough data for all species analyzed. The results reveal that the resin is not very selective for SO_4^{2-} removal from either pretreated Hanford supernate or Envelope B simulant. The breakthrough curve for flouride is the same as the curves for other (presumably) noninteracting ions (such as aluminate and NO_2^-). The F⁻ breakthough curve can be used as a baseline to represent the gradual breakthrough of feed solution from the column due to dilution with the liquid in the column headspace. The loading cycle was considered to start at the instant that feed was introduced to the tops of the columns. However, feed solution breakthrough occurred gradually due to mixing of the feed with the 1 M $NaNO_3$ solution, which was in the columns at the beginning of the loading cycle. Therefore, the 50% breakthrough points for each species analyzed should be decreased by the 50% breakthrough observed for the F⁻ in order to remove the effects of mixing on the observed breakthrough curves. The 50% F⁻ break-though point was observed at 1.5 CV for Hanford supernate and at 2.5 CV for Envelope B simulant. After correction for feed mixing, 50% SO_4^{2-} breakthrough was observed at 2.0 and 1.0 CV for column tests on Hanford supernate and Env. B simulant, respectively. The Cr 50% breakthrough point occurred at 2.5 and 1.5 CV for Hanford supernate and Env. B simulant, respectively. These observations indicate that CrO_4^- may interfere with SO_4^{2-} absorption by SuperLig® 655 resin. This result is consistent with the batch contact data which also indicated that Cr is removed by the resin. Based on the column data, the sulfate capacity of the ion exchange resin with Envelope B simulant was calculated to be 0.24 mmole SO_4^{2-}/ml of resin. Similarly, the pretreated Hanford supernate data gave a column capacity of 0.188 mmole SO_4^{2-}/ml of resin.

Relatively high concentrations of a proprietary material in the resin (PM1) were found in the first effluent samples collected from the columns. In the pretreated Hanford supernate, the PM1 concentration in the feed was 4 mg/L and the first column effluent sample contained 72 mg/L PM1 (after 1 CV of feed was processed). The first effluent sample collected from the simulant column (1 CV) contained 361 mg/L PM1, while the feed contained only 0.4 mg/L PM1. It appears that SuperLig® 655 resin leaches PM1 when contacted with caustic, sodium salt solutions. The PM1 concentration in the effluent quickly decreased to near 2 mg/L and remained fairly constant at this concentration for the remainder of the loading cycle. Leaching of PM1 likely leaves ligand sites that no longer exhibit the high selectivity for sulfate and chromate that had been observed in the Kd tests. Since PM1 is the origin of the sulfate selectivity, it appears that other common anions (e.g., chloride) are non-selectively removed by these ligands sites.

Table 3.5. Column Loading Data for SO_4^{2-} from Pretreated Hanford Supernate

Effluent (CV)	SO_4^{2-} (mg/L)	C/Co
Feed	5289	na
1	71	0.013
2	548	0.103
3	1804	0.341
4	3427	0.647
5	4328	0.817
6	4725	0.892
7	4869	0.919
8	5053	0.954
9	5186	0.979
10	4870	0.919

Table 3.6. Column Loading Data for SO_4^{2-} from Envelope B Simulant

Effluent (CV)	SO_4^{2-} (mg/L)	C/Co
Feed	8327	na
1	<50	<0.006
2	1185	0.142
3	3071	0.369
4	4661	0.560
5	5818	0.699
6	6633	0.797
7	6953	0.836
8	7010	0.842
9	7455	0.895

Figure 3.1. Column loading profile for SO4, PO4, Cr, Cl, and F from pretreated Hanford

Figure 3.2. Column loading profile for SO4, PO4, Cr, Cl, and F from Envelope B simulant (AZ-101)
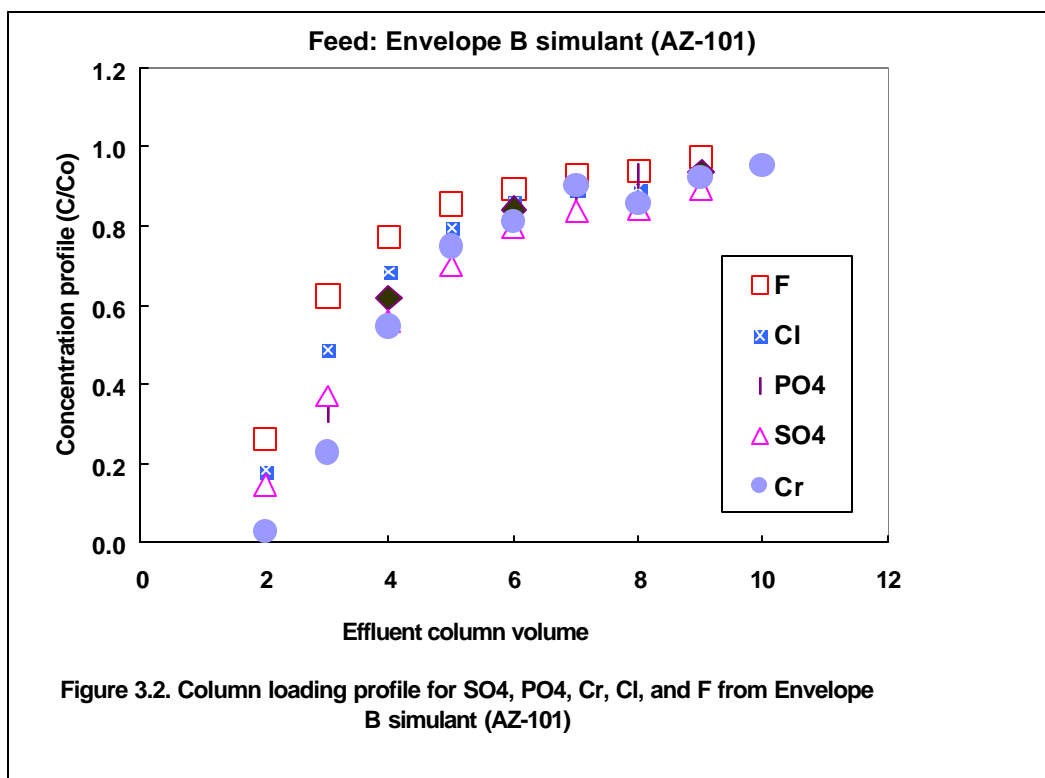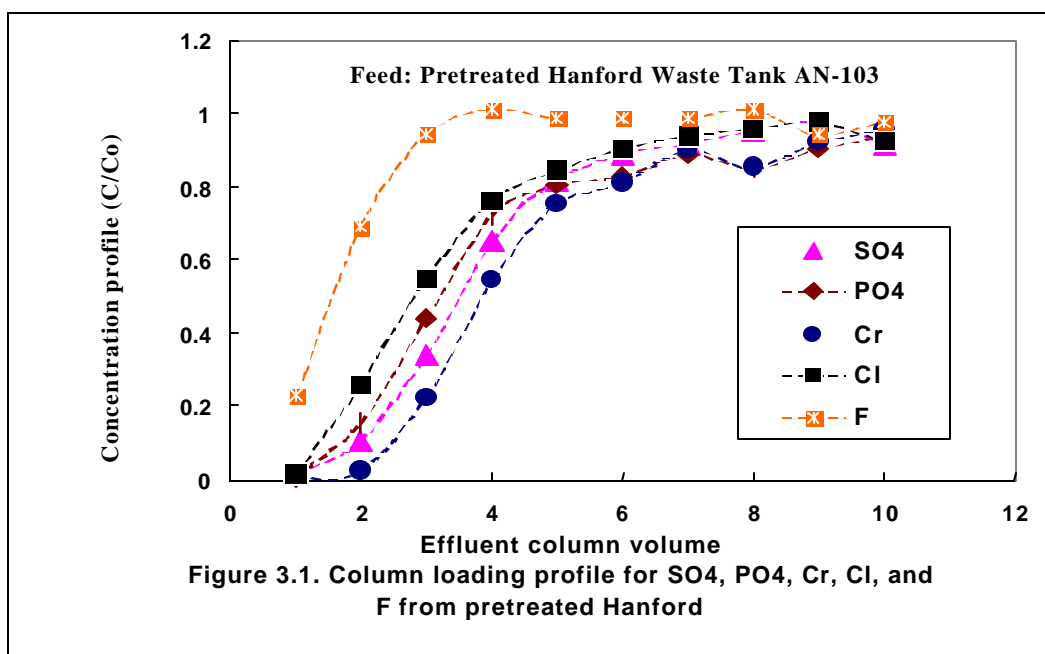
The elution of SO_4^{2-} from the ion exchange columns was performed with 0.5 M HNO_3 at a flow rate of 1 CV/h. The elution data for sulfate and chromium from pretreated Hanford supernate and Envelope B simulant are presented in Tables 3.7 and 3.8, respectively. The sulfate and chromium concentration profiles are plotted in Figures 3.3 and 3.4 for Hanford supernate and Envelope B simulant, respectively. Attachment 6 of Appendix 1 provides elution data for Envelope B simulant. Elution results for the two columns were similar. The highest sulfate concentration was observed in the first eluate sample but no significant peak was observed in the sulfate concentration. For the Hanford supernate column, the sulfate concentration remained at 1-2% of the feed concentration for the remainder of the elution. For the simulant column, the sulfate concentration decreased to below 1% of the feed after 3 CV of feed were processed. A Cr spike was observed at 3-4 CV for both columns. The chromium concentrations decreased rapidly after the peak was observed, but remained above 1% throughout the elution. ICP-ES analysis indicated that only trace amounts of PM1 were present in composited eluate samples.

Table 3.7. The elution data for SO_4^{2-} and Cr from pretreated Hanford supernate (AN-103)

Eluent CV	[SO_4^{2-}] (mg/L)	SO_4^{2-} C/Co	[Cr] (mg/L)	Cr C/Co
1	105	1.98E-02	3.01	4.30E-02
3	60	1.13E-02	7.66	1.09E-01
5	72	1.36E-02	2.57	3.67E-02
7	72	1.36E-02	2.28	3.26E-02
9	68	1.28E-02	1.66	2.37E-02

Pretreated Hanford supernate feed concentration: SO_4^{2-} = 5298 mg/L; Cr = 70 mg/L

Table 3.8. The elution data for SO_4^{2-} and Cr from Envelope B simulant (AZ-101)

Eluent CV	[SO_4^{2-}] (mg/L)	SO_4^{2-} C/Co	[Cr] (mg/L)	Cr C/Co
1	361	4.34E-02	37	5.43E-02
2	150	1.80E-02	28	4.11E-02
3	< 50	< 6.00E-03	89	1.30E-01
4	< 50	< 6.00E-03	100	1.47E-01
6	34	4.08E-03	76	1.11E-01
8	31	3.72E-03	39	5.72E-02
10	30	3.60E-03	24	3.52E-02

Envelope B simulant feed concentration: SO_4^{2-} = 8327 mg/L; Cr = 682 mg/L
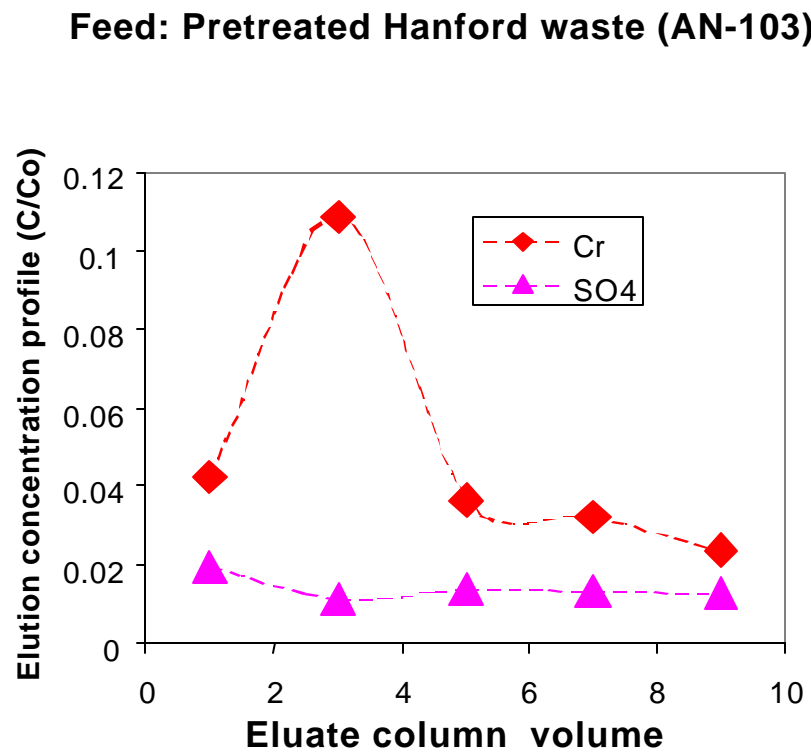
Figure 3.3. Column elution profile for SO4 and Cr from pretreated Hanford waste

Figure 3.4. Column elution profile for SO4 and Cr from Envelope B simulant
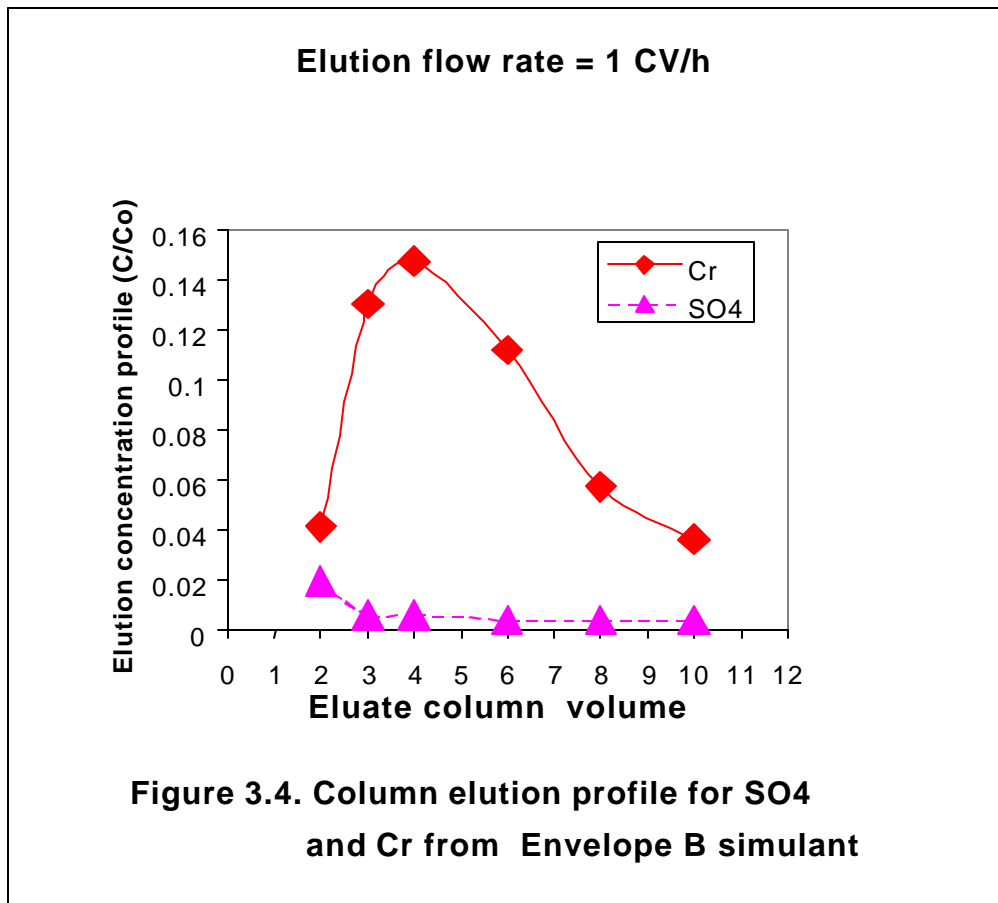
3.4   Conclusions

Sulfate removal testing was performed for pretreated Hanford supernate (Tank 241-AN-103) and Envelope B (Tank 241-AZ-101) simulant using SuperLig® 655 ion exchange resin. The results from the batch contact and column loading experiments indicated that the resin was ineffective for sulfate removal. The SO_4^{2-} K_d values for pretreated Hanford supernate and Envelope B simulant were 6.6 and 6.8 ml/g of resin, respectively; only 1 to 2 column volumes of pretreated Hanford supernate and Envelope B simulant were processed to reach the 50% SO_4^{2-} breakthrough point. The elution of sulfate was incomplete after 10 column volumes of 0.5 M nitric acid had passed through the columns at 1 CV/h. Data from the batch contact and column experiments suggest that CrO_4^- interferes with SO_4^{2-} removal. Relatively high levels of PM1 were observed in the first effluent samples collected from the columns. This PM1 is believed to have leached from the resin after contact with caustic, sodium salt solutions.

14

3.5   References

1.   King, W. D.; McCabe, D. J.; Hassan, N. M. *Evaluation of SuperLig® 639 Ion Exchange Resin for the Removal of Rhenium from Hanford Envelope A Simulant*, BNF-003- 98-0140, Rev. 0, April 13, 2000.

2.   Hassan, N. M.; King, W. D.; McCabe, D.J *Small-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tank 241-AN-103*, BNF-003-98-0146, Rev. 1, April 12, 2000.

3.   M. E. Johnson, River Protection Project Test Specification for Evaluating Sulfate Separation from LAW Solutions, Rev. 0, September 10, 1999.

4.0   Evaporation and Precipitation Scoping Tests

4.1   Introduction

The following describes the initial scoping tests investigating evaporation and precipitation methodologies for sulfate removal from Hanford waste Envelopes A, B, and C. The majority of the work was performed using simulants of these waste envelopes. A series of three hot beaker tests were also conducted with a waste sample from 241-AN-102 (Envelope C). The 241-AN-102 sample was a composite of samples generated from Sr/TRU precipitation tests.[1]

4.2   Experimental

Appendix 2 contains the analytical data and experimental conditions for each specific test. In general the scoping experiments were conducted in beakers using 25 mL of waste simulant solutions. The evaporations were carried out on a hot plate at a temperature to produce a mild boil. The evaporated solutions were allowed to cool to room temperature and filtered through a 0.45 μ disposable filter. Samples of the filtrate were then analyzed. The precipitation reactions using 25 mL of waste simulant solutions were carried out at room temperature unless a higher temperature was noted for specific tests in the tables of the appendix. The reactions were allowed to proceed for varying lengths of time (usually 1 hour), however, visual observation indicated the precipitations were nearly instantaneous. The reaction mixture was filtered through a 0.45 μ disposable filter at room temperature and the filtrate analyzed. The solids collected on the filter were washed with two small portions of 0.01 M NaOH to remove interstitial liquid. In some cases the solids were also washed with 1 M HNO_3 as noted in the tables in Appendix 2. Selected solids were analyzed for RCRA Toxicity using the standard Toxicity Characteristic Leaching Procedure (TCLP) test procedure.

Three beaker tests with an active sample of 241-AN-102 were carried out in the SRTC Shielded Cells. In the acid pre-strike experiment, 8.8 mL of concentrated nitric acid was added to 50 mL of the 241-AN-102 sample dropping the pH to ~3.8. Following the acid addition 21 mL of 0.25 M $Ba(NO_3)_2$ was added forming a precipitate. The precipitate was filtered and the solids washed on the filter with two 10 mL portions of 0.01 M NaOH. The filtrate and the combined wash solutions were analyzed. In the barium-only experiment, 152 mL of 0.25 M $Ba(NO_3)_2$ was added to 50 mL of the 241-AN-102 sample forming an immediate precipitate. The precipitate was filtered and the solids washed on the filter with two 10 mL portions of 0.01 M NaOH. The filtrate and the combined wash solutions were analyzed. In the calcium pre-strike experiment, 7 mL of 5 M $Ca(NO_3)_2$ was added to 50 mL of the 241-AN-102 sample forming an immediate precipitate. The precipitate was filtered from the solution and the solids washed on the filter with two 10 mL portions of 0.01 M NaOH. The filtrate was then treated with 21 mL of 0.25 M $Ba(NO_3)_2$ forming a precipitate. The precipitate was filtered from the solution and the solids washed on the filter with two 10 mL portions of 0.01 M NaOH. The final filtrate, the combined

wash solutions from the calcium precipitation, and the combined wash solutions from the barium precipitation were submitted for analysis. The program was terminated before obtaining analytical data from the calcium pre-strike experiment.

Analytical Development Section (ADS) of SRTC performed all analytical measurements. ADS uses the following analytical methods for determination of specific species. Nitrate, nitrite, sulfate, oxalate, phosphate, formate, chloride, and fluoride were measured by ion chromatography (IC). Chloride and fluoride were also determined by the ion selective electrode (ISE) method. Aluminate, carbonate, and hydroxide were measured using a titration method employing $SrCl_2$ to precipitate carbonate allowing the determination of all three species. Sodium, aluminum, and iron, as well as other metallic elements, were measured using inductively-coupled plasma-emission spectroscopy (ICP-ES). Potassium and mercury were measured using atomic adsorption spectroscopy (AA) with mercury determined using the cold-vapor technique (CV). Gamma emitting fission products were measured using gamma spectroscopy. Actinides were determined by inductively-coupled plasma mass spectrometry (ICP-MS) and alpha counting spectroscopy. Sr^{90} was determined from beta liquid scintillation counting.
The task specification identifies the data reporting and data quality requirements for the task.[3]

4.3   Results and Discussion

Initial scoping studies into the effectiveness of evaporation and/or precipitation were conducted on an Envelope B simulant. Table 4.1 shows the concentration of the major components of the Envelope B simulant. The Envelope B simulant, based on waste from 241-AZ-101, contains a high sulfate concentration (0.18 M).[2] The results in Tables 4.2 and 4.3 after evaporating the simulant by various amounts with or without the addition of precipitation additives indicate either insufficient sulfate removal or precipitation of a large quantity of other salts along with the sulfate. Calcium and strontium were chosen as precipitating agents due to the moderately low solubility of their sulfate salts. Although barium sulfates salts have a much lower solubility than calcium and strontium sulfates, barium was excluded at this point in the program as a precipitating agent due to regulatory concerns. As shown in Tables 4.4 and 4.5 the addition of various ratios of calcium or strontium to sulfate resulted in the same poor selectivity for sulfate regardless of the ratio applied. As the ratio of the precipitating agent to sulfate increases the amount of sulfate precipitated increases but so does the amount of other salts precipitated. The results presented in the tables show percent removal of each analyte for simplification. The percent removals were calculated on a mass basis:

(mg in original solution - mg in final solution) / mg in original solution x 100

Appendix 2 provides the complete data set for each experiment along with a description of the experiment.

With the limited success of calcium and strontium at selectively precipitating sulfate, the decision was made to explore the use of barium as a precipitating agent. A quick laboratory test showed that reagent grade barium sulfate passes the TCLP for barium indicating that the secondary waste produced from the precipitation might be non-hazardous potentially removing any regulatory concerns. The expectation was the very low solubility of barium sulfate would allow greater selectivity for sulfate precipitation.

Simulants for each of the three waste envelopes were tested with barium nitrate added as a solid and as a solution. Table 4.6 shows the concentrations of the major species for the Envelope A simulant, based on 241-AN-105 waste, and the Envelope C simulant based on 241-AN-107.[2] Tables 4.7 , 4.8, and 4.9 show the results of the reaction of barium nitrate with simulants of the three waste envelopes. The Envelope A simulant (Table 4.7) showed sufficient sulfate removal with the addition of a 0.2 M barium nitrate solution in 3:1 or greater molar ratio of barium to sulfate. The target for Envelope A of 3.87E-03 moles of sulfate per mole of sodium equates to ~55% sulfate removal for the Envelope A simulant. A large percentage of chromium and phosphate were also removed during the precipitation. Although a carbonate analysis was not conducted, due to difficulties measuring low levels of carbonate in the treated solutions, the majority of the carbonate was expected to have been removed from the simulant due to the low solubility of barium carbonate. The addition of solid barium nitrate proved much less effective at removing sulfate than the 0.2 M solution. Aside from the low selectivity, the other drawback of the barium nitrate solution method stems from the relatively low solubility of barium nitrate. The barium nitrate being soluble only to ~0.2 M in water leads to a 40% increase in the waste volume for the Envelope A simulant after treatment at the 3:1 barium to sulfate ratio. Heating the simulant to 60°C prior to addition of either the barium nitrate solution or barium nitrate solid made no discernable difference. In an effort to reduce the increase in waste volume caused by the addition of the dilute barium nitrate solution, the Envelope A simulant was first treated with a concentrated 6.0 M calcium nitrate solution (calcium pre-strike) with the intention of removing a majority of the carbonate ions and thereby allowing the use of less of the dilute barium nitrate solution. After the calcium pre-strike the addition of a 1:1 barium to sulfate molar ratio of the 0.2 M barium nitrate solution produced the required sulfate removal with only a 20% increase in liquid waste volume. However, the calcium pre-strike method removed even more of the other salts from the solution producing significantly more solids as compared to the addition of just the barium nitrate solution.

Sufficient sulfate removal from the Envelope B simulant was found with the addition of the 0.2 M barium nitrate solution at a barium to sulfate molar ratio of 1:1 or greater. As with the Envelope A simulant much of the chromium, phosphate, and presumably the carbonate were also removed. The sulfate removal target for Envelope B of 9.68E-03 moles of sulfate per mole of sodium equates to ~75% sulfate removal for the Envelope B simulant. The addition of the 0.2 M barium nitrate reagent at 60°C was not as effective. The addition of barium nitrate solid was also not as effective. The treatment of Envelope B simulant with 0.2 M barium nitrate at a 1:1 barium to sulfate molar ratio doubled the waste volume. Again in an effort to reduce the increase in waste volume a calcium pre-strike was used to remove carbonate prior to adding the dilute barium nitrate solution. The calcium pre-strike produced the required sulfate removal with a 60%

increase in waste volume. However, a large amount of other salts were also precipitated from the solution as was observed with the Envelope A simulant.

The sulfate removal from the Envelope C simulant was only effective using the 0.2 M barium nitrate solution with a high barium to sulfate molar ratio (see Table 4.9). The high concentration of carbonate in the simulant (see Table 4.6) requires enough barium to precipitate all of the carbonate and sulfate to achieve the desired level of sulfate removal. Predictably, due to the dilute barium nitrate reagent, this resulted in a large increase in waste volume (~6X). The use of a calcium pre-strike prior to the barium addition was effective in removing carbonate thereby reducing the required amount of sulfate and resulting in much less increase in liquid waste volume (~60%). However, the calcium pre-strike removed large quantities of other salts and therefore generated a large volume of solids. A nitric acid pre-strike was also attempted to reduce the volume of solids precipitated while also minimizing the increase in liquid waste volume. Prior to adding the barium nitrate solution, concentrated nitric acid was added to the waste to bring the pH to ~3-4 releasing the carbonate as carbon dioxide gas. After pH adjustment the 0.2 M barium nitrate solution was added in 1:1 barium to sulfate molar ratio. This procedure produced the required sulfate removal while minimizing the increase in liquid waste volume and the volume of solids produced. Although effective, the nitric acid pre-strike method generates a low pH waste stream untested with the current flowsheet model for evaporation and glass production. Readjusting the solution to a basic pH would result in a large increase in liquid waste volume. During the pH adjustment significant quantities of gas evolved raising concerns with foaming. Although no standing foam was observed with the Envelope C simulant, precipitation of salts, most likely aluminum, was observed. Most of the solids re-dissolved once the pH dropped below ~3.5.

Table 4.10 shows the results of further testing of the Envelope C simulant with barium solutions using calcium and acid pre-strikes. The Envelope C waste presents the most difficulty due to the high levels of carbonate removed by the barium leading to large increase in liquid waste volume. In the first two tests listed in the table in which a 0.2 M barium nitrate solution was used the liquid waste volume increased by ~60 -70%. A more concentrated barium reagent, 1.5 M barium nitrite was used in the last three tests and proved as effective in removing sulfate and only increased the liquid waste volume by ~20%.

The precipitated solids produced from select experiments in Tables 4.7, 4.8, 4.9, and 4.10 were tested for hazardous characteristics using the TCLP method. In each case the solids were separated from the reaction mixture using filtration and the solids washed on the filter with inhibited water (0.01 M NaOH) to flush interstitial supernatant liquid. In all cases the results of the leaching procedure indicated the solids were non-hazardous for chromium (5 mg/L limit in the leach solution), however all but one test failed for barium (100 mg/L limit in the leach solution) indicating that without further treatment the solids produced from the barium precipitation would be handled as hazardous waste. The experiment that produced a non-hazardous precipitate was an acid pre-strike on the Envelope C simulant with the solids washed with inhibited water (0.01 M NaOH) followed by 1.0 M nitric acid to remove barium carbonate and any unreacted barium nitrate. However, several other tests in which the solids were washed with inhibited water and nitric acid still failed the TCLP for barium. Since reagent grade barium

sulfate was found to pass the TCLP procedure, unreacted barium nitrate and the presence of barium carbonate in the precipitated solids were suspected of causing the failure to meet TCLP limits for barium.

Small scale beaker tests with an active (radioactive) sample of 241-AN-102 that had been pretreated to remove Sr/TRU were conducted using barium precipitation with an acid pre-strike, a calcium pre-strike, and with barium nitrate with no pre-strike. The sulfate removal program was terminated prior to collecting analytical data on the calcium pre-strike test. The results of the beaker tests with only barium precipitation and with an acid pre-strike in Table 4.11 produced the required sulfate removal based on the lower detection limit for sulfate ion. The test results mimic those obtained with the Envelope C simulant discussed previously. The data in Table 4.11 also indicate that large amounts of TRU radionuclides were removed in both precipitations.

4.4   Conclusions

Although several of the scoping tests yielded the required level of sulfate removal significant problems exist for use in a large scale process. The poor selectivity for sulfate with all of the methods produces large volumes of solids or large increases in liquid waste volume or both. The barium precipitation process showed the most promise but also suffers from poor selectivity. In addition the solids produced from the barium precipitations would require handling and disposal as hazardous and possibly TRU waste.

4.5   References

1.   S. W. Rosencrance, R. A. Dewberry, D. P. Diprete, T. B. Edwards, S. J. Emory, C. A. Nash, S. C. Smith, W. R. Wilmarth, "Precipitation Results for AN-102: A Statistically Designed Approach to Evalute Filterability and Sr/TRU Decontamination", BNF-003-98-0161, Septmeber 31, 1998, Westinghouse Savannah River Company, Aiken SC.

2.   R. E. Eibling and C. A. Nash, "Hanford Waste Simulants Created to Support the Research and Development on the River Protection Project – Waste Treatment Plant", Draft Report, WSRC-TR-2000-00338, SRT-RPP-2000-00017, Westinghouse Savannah River Company, Aiken, SC.

3.   M. E. Johnson, River Protection Project Test Specification for Evaluating Sulfate Separation from LAW Solutions, TSP-W375-99-00012, Rev. 0, September 10, 1999.

Table 4.1. Composition of the Envelope B Simulant.

	M	**mg/L**
$[SO_4^{2-}]$	0.18	1.77E+04
$[NO_3^-]$	1.22	7.56E+04
$[NO_2^-]$	1.41	6.51E+04
$[PO_4^{3-}]$	0.02	1.50E+03
$[Cl^-]$	0.01	2.00E+02
$[F^-]$	0.10	1.81E+03
$[CO_3^{2-}]$	0.38	2.31E+04
$[OH^-]$	2.12	3.60E+04
Na	4.74	1.09E+05
K	0.12	4.62E+03
Al	0.40	1.07E+04
Cr	0.01	7.30E+02

Envelope B simulant based on composition of waste from tank 241-AZ-101.

Table 4.2. Results of Initial Scoping Tests of Evaporation and/or Precipitation of the Envelope B Simulant. Values are the Percent of Each Species Removed from the Simulant.

Experiment	$[SO_4^{2-}]$	$[NO_3^-]$	$[NO_2^-]$	$[PO_4^{3-}]$	$[Cl^-]$	$[F^-]$
25% Evaporation	-3%	-4%	-2%	-2%	20%	26%
50% Evaporation	86%	-35%	-26%	85%	23%	>99%
25% Evaporation +Lime	37%	-13%	-11%	-9%	17%	70%
50% Evaporation +Lime	69%	-23%	-16%	86%	26%	99%
Solid Ca(OH)$_2$	14%	-100%	-94%	96%	-21%	98%
20% Evaporation + Solid Ca(OH)$_2$	1%	-1%	0%	73%	27%	62%
40% Evaporation + Solid Ca(OH)$_2$	15%	-7%	-4%	88%	31%	92%
50% Evaporation + Solid Ca(OH)$_2$	51%	51%	50%	55%	51%	54%
SrCl$_2$	1%	-2%	-2%	11%	-2357%	27%
30% Evaporation + Solid SrCl$_2$	21%	-6%	-5%	7%	-5166%	-36%
50% Evaporation + Solid SrCl$_2$	64%	-11%	-7%	13%	-5339%	43%
SrCl$_2$ Solution	30%	27%	25%	86%	-5887%	32%

- Sulfate removal of ~75% required to meet the target sulfate to sodium ratio of 9.68E-03 for the Envelope B simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

Table 4.3. Results of Scoping Tests of Evaporation and/or Precipitation of the Envelope B Simulant. Values are the Percent of Each Species Removed from the Simulant.

	$[SO_4^{2-}]$	$[NO_3^-]$	$[NO_2^-]$	$[PO_4^{3-}]$	$[Cl^-]$	$[F]$	Al	Cr	Na	K
20% Evaporation	11%	-13%	-11%	-9%	13%	56%	-7%	-6%	-2%	-2%
30% Evaporation	30%	-13%	-11%	-4%	24%	90%	-4%	-1%	7%	0%
40% Evaporation	44%	3%	3%	13%	-7%	59%	8%	10%	17%	13%
50% Evaporation	55%	10%	11%	39%	>94%	>99%	12%	17%	23%	16%
60% Evaporation	71%	21%	22%	68%	13%	86%	26%	27%	35%	28%
30% Evaporation + $Sr(NO_3)_2$	39%	-27%	5%	7%	32%	87%	9%	11%	16%	15%
50% Evaporation + $Sr(NO_3)_2$	50%	-34%	2%	20%	0%	83%	11%	17%	24%	13%
30% Evaporation + $SrCl_2$	45%	23%	22%	28%	-4279%	76%	20%	22%	26%	24%
50% Evaporation + $SrCl_2$	59%	20%	20%	45%	-4561%	>99%	23%	25%	31%	26%

- Strontium added at a 1:1 molar ratio to sulfate in all experiments.

- Sulfate removal of ~75% required to meet the target sulfate to sodium ratio of 9.68E-03 for the Envelope B simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

Table 4.4. Addition of a 5.0 M Calcium Nitrate Solution to the Envelope B Simulant at Various Calcium to Sulfate Molar Ratios. Values are the Percent of Each Species Removed from the Simulant.

	Ca:SO$_4^{2-}$	[SO$_4^{2-}$]	[NO$_3^-$]	[NO$_2^-$]	[PO$_4^{3-}$]	[Cl$^-$]	[F]	Al	Ca	Cr
Test 1	0.47	2%	-13%	-1%	13%	10%	11%	2%	-94%	0%
Test. 2	0.95	8%	-28%	3%	44%	17%	38%	12%	36%	7%
Test. 3	1.42	5%	-41%	-1%	56%	4%	57%	45%	>79%	-2%
Test. 4	1.90	12%	-68%	-1%	86%	27%	81%	40%	>78%	3%
Test. 5	2.37	17%	-88%	-2%	94%	26%	84%	58%	>78%	3%
Test. 6	2.85	24%	-102%	-2%	96%	28%	89%	65%	>78%	6%
Test. 7	4.75	57%	-175%	-9%	>94%	29%	91%	89%	68%	18%
Test. 8	14.2	100%	-589%	-8%	>92%	>18%	>96%	ND	ND	ND

- Sulfate removal of ~75% required to meet the target sulfate to sodium ratio of 9.68E-03 for the Envelope B simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

- ND = not determined

Table 4.5. Addition of a 2.3 M Strontium Nitrate Solution to the Envelope B Simulant at Various Strontium to Sulfate Molar Ratios. Values are the Percent of Each Species Removed from the Simulant.

	Sr:SO$_4^{2-}$	[SO$_4^{2-}$]	[NO$_3^-$]	[NO$_2^-$]	[PO$_4^{3-}$]	[Cl$^-$]	[F]
Test 1	0.22	1%	-6%	4%	28%	-6%	18%
Test 2	0.44	2%	-19%	0%	47%	-8%	39%
Test 3	0.88	-1%	-37%	-2%	49%	8%	69%
Test 4	1.32	2%	-55%	0%	72%	8%	87%
Test 5	1.76	5%	-71%	2%	85%	19%	96%
Test 6	2.20	7%	-91%	0%	96%	29%	97%
Test 7*	1.32	0%	-57%	0%	45%	42%	34%
Test 8	6.8	93%	-292%	-7%	92%	18%	96%

* Envelope B Simulant solution was heated to 95°C prior to addition of the strontium nitrate solution.

- Sulfate removal of ~75% required to meet the target sulfate to sodium ratio of 9.68E-03 for the Envelope B simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

Table 4.6. Compositions of the Envelope A and Envelope C Simulants

	Envelope A Simulant		Envelope C Simulant	
	M	mg/L	M	mg/L
$[SO_4^{2-}]$	2.82E-02	2.71E+03	6.86E-02	6.59E+03
$[NO_3^-]$	1.60E+00	9.90E+04	2.98E+00	1.85E+05
$[NO_2^-]$	1.28E+00	5.87E+04	1.06E+00	4.87E+04
$[PO_4^{3-}]$	1.22E-02	1.16E+03	9.33E-03	8.86E+02
$[C_2O_4^{2-}]$	5.22E-03	4.60E+02	7.49E-03	6.59E+02
$[OH^-]$	1.50E+00	2.55E+04	5.02E-01	8.53E+03
$[CO_3^{2-}]$	7.08E-02	4.25E+03	1.12E+00	6.70E+04
$[Cl^-]$	1.20E-01	4.25E+03	4.12E-02	1.46E+03
$[F^-]$	2.50E-02	4.75E+02	5.59E-03	1.06E+02
Al	5.72E-01	1.54E+04	1.14E-02	3.08E+02
Ca	4.66E-04	1.87E+01	1.18E-02	4.72E+02
Cr	1.21E-02	6.31E+02	2.70E-03	1.40E+02
K	8.92E-02	3.49E+03	3.70E-02	1.44E+03
Na	4.74E+00	1.09E+05	7.04E+00	1.62E+05
P	1.22E-02	3.79E+02	9.33E-03	2.89E+02
S	2.82E-02	9.03E+02	6.86E-02	2.20E+03

Envelope A simulant based on composition of waste from tank 241-AN-105.

Envelope C simulant based on composition of waste from tank 241-AN-107.

Table 4.7. Addition of a 0.2 M Barium Nitrate Solution to the Envelope A Simulant at Various Barium to Sulfate Molar Ratios. Values are the Percent of Each Species Removed from the Simulant.

Reagent	Ba:SO$_4^{2-}$	[SO$_4^{2-}$]	[NO$_3^-$]	[NO$_2^-$]	[PO$_4^{3-}$]	[Cl$^-$]	[F]	Al	Cr	P	S
0.15 M Ba(NO$_3$)$_2$ Solution	1:1	26%	-5%	-6%	13%	-2%	0%	0%	81%	22%	28%
0.2 M Ba(NO$_3$)$_2$ Solution	3:1	57%	-13%	-7%	20%	-7%	8%	2%	87%	40%	59%
0.2 M Ba(NO$_3$)$_2$ Solution	5:1	70%	-16%	-4%	36%	-9%	10%	4%	96%	61%	73%
Ba(NO$_3$)$_2$ Solid added to Simulant at 60°C	1:1	19%	-5%	-2%	-1%	-3%	-1%	-3%	63%	5%	32%
0.2 M Ba(NO$_3$)$_2$ Solution added to Simulant at 60°C	1:1	29%	-1%	3%	2%	1%	9%	2%	78%	15%	51%
0.3 M Ba(NO$_3$)$_2$ Solution added to Simulant After Calcium Nitrate Prestrike*	1:1	62%	0%	13%	72%	7%	76%	13%	80%	32%	49%

- Sulfate removal of ~55% required to meet target sulfate to sodium ratio of 3.87E-03 for the Envelope A simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

* The 0.3 M concentration was calculated from the weight of Ba(NO$_3$)$_2$ solid added to a small portion of water. With the small quantities involved no solids were observed, however, all of the Ba(NO$_3$)$_2$ solids probably were not dissolved.

Table 4.8. Addition of a 0.2 M Barium Nitrate Solution to the Envelope B Simulant at Various Barium to Sulfate Molar Ratios. Values are the Percent of Each Species Removed from the Simulant.

Reagent	Ba:SO$_4^{2-}$	[SO$_4^{2-}$]	[NO$_3^-$]	[NO$_2^-$]	[PO$_4^{3-}$]	[Cl$^-$]	[F]	Al	Cr	P	S
0.2 M Ba(NO$_3$)$_2$ Solution	1:1	86%	-77%	-10%	41%	-16%	-56%	0%	93%	35%	86%
0.3 M Ba(NO$_3$)$_2$ Solution*	1:1	84%	-34%	-6%	14%	-7%	-26%	-1%	92%	27%	84%
0.2 M Ba(NO$_3$)$_2$ Solution	3:1	97%	-144%	-3%	94%	-2%	-84%	8%	99%	92%	97%
0.3 M Ba(NO$_3$)$_2$ Solution*	3:1	93%	-100%	-6%	44%	-40%	-56%	0%	97%	81%	93%
0.3 M Ba(NO$_3$)$_2$ Solution*	5:1	97%	-164%	-6%	<67%	-74%	11%	-4%	100%	100%	100%
0.7 M Ba(NO$_3$)$_2$ Solution added to Simulant at 60°C*	1:1	69%	-18%	7%	-8%	-1%	3%	7%	83%	-16%	73%
Ba(NO$_3$)$_2$ Solid added to Simulant	1:1	40%	-25%	-3%	10%	7%	-3%	3%	53%	13%	43%
Ba(NO$_3$)$_2$ Solid added to Simulant at 60°C	1:1	64%	-24%	-1%	-12%	-3%	7%	1%	85%	-34%	67%
0.2 M Ba(NO$_3$)$_2$ Solution added to Simulant After Calcium Nitrate Prestrike	1:1	78%	-91%	-6%	<86%	-57%	54%	19%	89%	99%	76%

- Sulfate removal of ~75% required to meet target sulfate to sodium ratio of 9.68E-03 for the Envelope B simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

* The 0.3 M and 0.7 M concentrations were calculated from the weight of Ba(NO$_3$)$_2$ solid added to a small portion of water. With the small quantities involved no solids were observed, however, all of the Ba(NO$_3$)$_2$ solids probably were not dissolved.

Table 4.9. Addition of a 0.2 M Barium Nitrate Solution to the Envelope C Simulant at Various Barium to Sulfate Molar Ratios. Values are the Percent of Each Species Removed from the Simulant.

Reagent	Ba:SO_4^{2-}	[SO_4^{2-}]	[NO_3^-]	[NO_2^-]	[PO_4^{3-}]	[Cl^-]	[F]	Al	Cr	P	S
0.2 M Ba(NO$_3$)$_2$ Solution	5:1	3%	-18%	3%	-3%	7%	8%	27%	26%	36%	11%
0.2 M Ba(NO$_3$)$_2$ Solution	10:1	13%	-45%	6%	-3%	2%	14%	37%	47%	68%	15%
0.2 M Ba(NO$_3$)$_2$ Solution	17:1	77%	-86%	5%	-16%	-14%	14%	55%	66%	98%	87%
0.2 M Ba(NO$_3$)$_2$ Solution added to Simulant After Calcium Nitrate Prestrike	1:1	68%	-75%	9%	-48%	-25%	39%	57%	60%	100%	96%
0.2 M Ba(NO$_3$)$_2$ Solution added to Simulant After Nitric Acid Prestrike	1:1	71%	-91%	44%	71%	-25%	26%	7%	7%	14%	72%

- Sulfate removal of ~60% required to meet target sulfate to sodium ratio of 4.55E-03 for the Envelope C simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

Table 4.10. Addition of 0.2 M Barium Nitrate and 1.5 M Barium Nitrite Solutions to the Envelope C Simulant with Calcium and Acid Pre-Strikes. Values are the Percent of Each Species Removed from the Simulant.

Reagent	Ba:SO$_4^{2-}$	S	Al	Cr	P
0.2 M Ba(NO$_3$)$_2$ Solution added to Simulant After Nitric Acid Prestrike	1.3:1	96%	3%	12%	20%
0.2 M Ba(NO$_3$)$_2$ Solution added to Simulant After Calcium Nitrate Prestrike	1.3:1	98%	78%	69%	99%
1.5 M Ba(NO$_2$)$_2$ Solution added to Simulant After Nitric Acid Prestrike	0.8:1	83%	31%	10%	43%
1.5 M Ba(NO$_2$)$_2$ Solution added to Simulant After Nitric Acid Prestrike	1.5:1	97%	32%	13%	55%
1.5 M Ba(NO$_2$)$_2$ Solution added to Simulant After Nitric Acid Prestrike	1.5:1	99%	10%	0%	26%

- Sulfate removal of ~60% required to meet target sulfate to sodium ratio of 4.55E-03 for the Envelope C simulant.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

Table 4.11. Sulfate Removal Beaker Test of a Radioactive Sample from 241-AN-102 (Envelope C) using 0.2 M Barium Nitrate with and without an Acid Pre-Strike. Values Represent the Percent of Each Species Removed from the Sample.

	Acid Pre-strike Prior to Barium Precipitation	Barium Only Precipitation
$[NO_3^-]$	-127%	-59%
$[NO_2^-]$	57%	-8%
$[SO_4^{2-}]$	>63.5%	>91.0%
$[Cl^-]$	16%	-2%
$[F^-]$	14%	5%
Al	56%	6%
Ca	18%	54%
Cr	46%	ND
Na	5%	7%
P	62%	93%
Cs^{137}	11%	10%
Pu^{238}	28%	6%
$Pu^{239/240}$	7%	-217%
Cm^{244}	89%	91%
Am^{241}	33%	90%
Sr^{90}	89%	99%
U^{235}	-13%	ND
U^{238}	0%	ND
Pu^{239}	14%	ND
Tc^{99}	-17%	-8%

ND - not detected

- Sulfate removal of ~60% required to meet target sulfate to sodium ratio of 4.55E-03 for the Envelope C 241-AN-102 sample.

- Negative values of percent removed indicate an increase in concentration possibly due to impurities present in added reagents or analytical and experimental error.

5.0   Sulfate Precipitation of 241-AN-102 (Small C)

5.1   Introduction

Sulfate precipitation tests with barium were performed with pretreated AN-102 (small C) sample. The AN-102 sample had previously undergone pretreatment process testing to separate Sr/TRU, Cs, and Tc.[1] Approximately 230-ml of the pretreated small C(AN-102) solution had previously been processed to separate these radionuclides. The primary objective of this test is to provide information on sulfate separation from the small C (AN-102) sample. The secondary objective is to remove sufficient sulfate from the AN-102 sample in preparation for vitrification in a small crucible. The sulfate precipitation results will be used to model the precipitation system to determine design parameters. Therefore, the success criteria for these tests are to accurately measure the concentration of all analytes and radionuclides (±15% reproducibility) in the starting solution, filtrates, and precipitates. This will facilitate quantitative determinations and mass balances for sulfate in the system.

5.2   Experimental

The materials used for the precipitation tests were as follows:

    1.   Pretreated AN-102 (small C).

    2.   0.25 M barium nitrate

    3.   0.01 M sodium hydroxide (inhibited water).

    4.   De-mineralized water.

    5.   Dilute nitric acid solutions (0.5 and 1 M)

The precipitation test with barium nitrate was conducted using a pretreated small C (AN-102) sample. The precipitation test was performed under approved test specification and task and technical assurance plans.[2,3] A small volume (230 mL) of pretreated AN-102 sample was used for the precipitation tests. The sample had previously undergone pretreatment process testing to separate Sr/TRU, Cs, and Tc. In the precipitation test, the AN-102 pretreated solution was carefully transferred into a 1-L graduated mixing vessel designed for the experiment. A 76-mm stirring bar was placed in the bottom of the mixing vessel prior to solution transfer. The AN-102 solution was continuously mixed by turning the stirrer on. The mixing continued while the solution temperature was ascertained at 20 °C. About 622 mL of 0.25 M barium nitrate solution was carefully added to the mixing vessel. The addition of barium nitrate directly into the mixing vessel was evenly distributed and it lasted 30 minutes. The mixing of the solution continued one hour past the final addition of barium nitrate. The stirrer bar was then turned off and the settling rate of the barium precipitate was recorded via the mixing vessel graduations in cm per minute every 10 minute interval for a total of 2 hours.

The settled barium precipitate cake was re-suspend by gently stirring the slurry. A small sub-sample of the slurry (20 mL) was taken and analyzed for weight percent insoluble solids, viscosity versus shear rate, density, and particle size distribution. A small portion of the remaining slurry was filtered under vacuum using 0.45-µm Nalgene filter element. The filter flux was recorded for the first minute, after which the vacuum was turned off. Approximately 8 g of cake was found on the filter top after approximately 34 seconds. The liquid (filtrate) collected in the filter bottom was ~ 150 mL in the first 34 seconds. The filtration of the remaining slurry was continued and at the end, the mass of the precipitate (cake) on the filter top and the volume of liquid (filtrate) collected on the filter bottom were 45.4 g and 810 mL, respectively. A sub-sample of the damp precipitate was analyzed for particle size distribution and a sub-sample of the filtrate (liquid) was analyzed to determine the concentration of all analytes and radionuclides.

The barium precipitate was twice washed with with 2:1 volume ratio of inhibited water (i.e. 0.01M NaOH solution); the wash solutions were collected separately. The solid was first transferred into a beaker and slurried with the first wash solution (80 mL of 0.01 M NaOH). The sodium hydroxide was slowly added into the beaker while stirring the solution. The slurry was then transferred into the filter element under vacuum. The filtration was complete in 36 seconds and produced 43.13 g of damp cake and 80 mL of liquid (filtrate). The second wash solution was performed in the same manner. The second wash also used 80 mL of 0.01 M NaOH. After filtration, 43.0 g of solids were produced on the filter top and 80 mL of filtrate (liquid) was collected in the filter bottom. The filtration of the second slurry was complete in 37 seconds. Sub-samples (5 mL) of the wash solutions were submitted for analysis to determine the concentration of all analytes and radionuclides.

The washed barium precipitate was rinsed with a 3:1 volume ratio of de-mineralized water. The solid cake was transferred into a beaker and slurried with 120 mL of de-mineralized water. The slurry was transferred into a 0.45 µ filter element. This first water rinse produced 43 g of solid and 112 mL of liquid (filtrate). The filtration was complete in 49 seconds. The rinse and inhibited water wash solutions were kept separate from the AN-102 filtrate collected at the beginning of the precipitation process. A sub-sample of the solid collected during wash and rinse steps was dried at 105 °C and submitted for analysis to determine the particle size distribution.

The barium precipitate cake was washed twice with a 2:1 volume ratio of 0.5 M nitric acid. The acid was used to re-suspend the solid cake from the previously used filter tops. The first acid wash used 80 mL of nitric acid to dissolve the solid transferred into a beaker. The slurry was transferred into a filter element under vacuum. The filtration produced 40.3 g of cake and 79 mL of liquid (filtrate). The second acid wash, which was conducted in the same manner as the previous acid wash, also used 80 mL of 0.5 M nitric acid to dissolve solid cake. After dissolution and filtration, the solid collected on the filter top was 34.6 g and the liquid collected in the filter bottom was 80 mL. The entire filtration for the first acid wash was 26 vs. 43 seconds for the second acid wash. The second acid wash was followed by water rinse using a 3:1 volume ratio of de-mineralized water. The post acid water rinse used 90 mL of de-mineralized water for

slurrying solid and, after filtration, resulted 30.8 g solid cake on filter top. The liquid (filtrate) collected in the filter bottom was 89 mL. The filtration for the de-mineralized water rinse step was complete in 44 seconds. The acid wash and de-mineralized water rinse solutions were kept separate from the AN-102 filtrate.

After the second acid wash, the solid was scraped from the filter top and transferred into a beaker.

The solid cake was slurried with 150 mL of 1 M nitric acid. The acid was added very slowly into the beaker while gently stirring the solution. The filtration of this acid wash produced 13.7 g of solid on the filter top and 100 mL of liquid (filtrate) , which was collected in the filter bottom. The solid cake on the filter top appeared gummy. This acid wash was also followed by a water rinse using 120 mL de-mineralized water, which resulted in a net 8.5 g cake on the filter top and 80 ml of liquid (filtrate) in the filter bottom.

A fourth and final acid wash of the solid was performed again with 0.5 M nitric acid. The solid from the previous filtration was transferred into a beaker. The acid (80 mL) was slowly added into the beaker while gently stirring the solution. The filtration of the resulting slurry was complete in 4 minutes and 17 seconds. The weight of filter cake was 6.9 g and the volume of liquid collected in filter bottom was 80 mL. The cake was rinsed with 115 mL of de-mineralized water, which resulted a net 6.2 g solid cake.

The 0.01 M NaOH water wash and the accompanying de-mineralized water rinse solutions were transferred into 2-L flask. The AN-102 filtrate collected from first filtration of the barium precipitate slurry was added very slowly while continuously mixing the solution. The combined volume of the AN-102 filtrate and 0.01 M NaOH wash and accompanying de-mineralized water rinse was 1025 mL. This composited AN-102 filtrate (product) was sampled to determine the concentration of all analytes and radionuclides. The product was provided for evaporation and vitrification tests.

The test specification and task plan state the requirements for data reporting and data quality.[2,3]

5.3   Results and Discussion

Preliminary test results of sulfate precipitation from pretreated AN-102 (small C) with direct barium nitrate addition are provided in Tables 5.1-5.5. A total of 810 mL of filtrate was generated from the the treatment of 230 mL of AN-102 with 622 mL of 0.20 M Barium nitrate solution. The mass of barium precipitate cake (damp mass) produced from filtration of the barium precipitation slurry was 45.4 g. The initial dead-end filter flux for the barium precipitate slurry using a 0.45 μm filter element under vacuum was 1.44 gpm/ft^2. The composited volume of the AN-102 filtrate and accompanying 0.01 NaOH and water wash solutions was 1025 mL. The density and total weight percent solids in the composited filtrate (product) were 1.069 g/mL and 8.74% wt., respectively. The filtrate from the barium precipitate

slurry and the composited filtrate (product) were analyzed for metals, radionuclides, and total organic carbon and the data are presented in Table 1, along with the pretreated AN-102 sample. The amount of sulfate and other anions in the filtrate are also provided in Table 5.1. The filter cake (barium precipitate) was washed twice with 0.01 M NaOH solution, followed by water rinse, 0.5 and 1.0 M nitric acid and accompanying water rinse to displace interstitial liquid, caustic, and dissolved carbonate, respectively. The 0.01 M NaOH wash and accompanying water rinse solutions were analyzed for metals and gamma emitting radionuclides and the results are presented in Table 5.2. The dead-end filter flux for the 0.01 M NaOH wash using a 0.45 μm filter element under vacuum was 6.60 gpm/ft^2. The nitric acid wash and accompanying water rinse solutions were also analyzed for metals and gamma emitting radionuclides and the results are presented in Table 5.3. The alpha-emitting radionuclides in barium precipitate slurry, composite filtrate product, 0.01 M NaOH wash, water rinse, and 0.5 M nitric acid wash and accompanying water rinse are presented in Table 5.4. Table 5.5 shows the particle size of solids in the barium precipitate slurry and the filter cake after initial washes with 0.01 M NaOH and with 0.5 M nitric acid.

5.4   Conclusions

A sulfate removal from pretreated small C (AN-102) by precipitation with barium nitrate was conducted to provide feed material for evaporation and vitrification tests. The small C sample had previously undergone pretreatment processes to remove Sr/TRU, Cs, and Tc. The test demonstrated that up to 97.8% of sulfate can be removed from pretreated small C (AN-102) by precipitation with barium nitrate.However, the treament also removed 86% of the carbonate (based on TIC analysis), 93% of the phosphate, and 86% of the chromate, along with smaller percentages of many other species. The test produced 1025 mL of filtrate product for downstream evaporation and vitrification tests.

5.5 References

1. N. M. Hassan, D. J. McCabe, and W. D. King, Small-Scale Ion Exchange Removal of Cesium and Technetium From Hanford Tank 241-AN-102, BNF-003-0219, Revision 0, March 29, 2000.

2. A. Elsden, M. E. Johnson, and E. Slaathaug, Test Specifications for Separating Sulfate from Pretreated AN-107, AZ-102, and AN-102 solutions by Precipitation, TSP-W375-99-00016, Rev. 0, January 4, 2000.

3. S. W. Rosencrane, M. S. Hay, N. M. Hassan, C. Coleman, Task Technical and Quality Assurance Plan for Small C sulfate Removal Test, BNF-003-98-2040, Rev. 0. January 14, 2000.

Table 5.1. Characterization of pretreated AN-102 (Small C)

Sample ID		before precipitation (avg. duplicate values)		Barium precipitation filtrate of AN-102		Composited filtrate (product*)
Cs-137 (µCi/mL)		1.06E-01		1.88E-02		1.40E-02
Co-60 (µCi/mL)		4.14E-02		1.08E-04		1.06E-04
Eu-154 (µCi/mL)		2.93E-02		1.28E-04		1.09E-04
Eu-155 (µCi/mL)		1.77E-02		2.11E-04		1.86E-04
ICP-MS, mg/L						
mass Tc-99		2.54E+00		5.81E-01		5.81E-01
massTh-232,		9.65E-01				
mass U-233	<	7.17E-04				
mass U-235	<	7.17E-04				
mass U-236	<	7.17E-04				
mass Np-237		8.02E-02				
mass Pu/U-238		6.21E-01				
mass Pu-239		3.06E-02				
mass Pu-240	<	7.17E-04				
mass Am/Pu-241	<	7.17E-04				
mass Am-243	<	7.17E-04				
mass Cm-245	<	7.17E-04				
AA, mg/L						
K		9.12E+02		2.45E+02		2.10E+02
SE		Nm		1.91E-01		1.58E-01
AS		Nm		5.26E-02		4.34E-02
Hg		Nm	<	1.10E-01	<	1.10E-01
IC, mg/L						
NO_3		9.00E+04		5.36E+04		4.03E+04
NO_2		3.70E+04		8.78E+03		6.76E+03
PO_4		2.00E+03	<	1.00E+02	<	1.00E+02
SO_4		5.84E+03		3.50E+01		3.50E+01
Oxalate		9.08E+02		1.59E+02		1.20E+02
Formate		4.76E+03		1.34E+03		1.02E+03
Cl-		1.58E+03		3.74E+02		2.84E+02
F-		6.72E+02		2.0E+02		1.58E+02
Inorganic (TIC)		6.62E+03		2.70E+02		4.16E+02
Organic (TOC)		2.87E+04		3.81E+03		3.304E+03
OH^- (Free)		8.3E-01		1.88E-01		1.88E-01
ICP-ES, mg/L						
Al		6.57E+03		1.82E+03		1.42E+03
B		2.21E+01		4.85E+00		3.76E+00
Ba	<	1.11E+00		7.234E+02		6.53E+03
Ca		2.02E+02		1.62E+01		1.44E+01
Cd		2.52E+01		6.44E+00		5.54E+00
Co	<	3.32E+00		6.16E-01		4.55E-01
Cr		6.81E+01		2.73E+00		2.02E+00
Cu		6.17E+00		2.07E+00		1.70E+00

Fe		3.52E+00		4.69E-01		4.13E-01
La	<	4.42E+00	<	1.00E+00		1.00E+00
Li	<	1.66E+00	<	1.82E-01		1.82E-01
Mg		3.00E+00		9.5E-02		1.00E-01
Mn	<	5.53E-01	<	9.10E-02		9.10E-02
Mo		2.94E+01		6.88E+00		5.28E+00
Na		1.20E+05		3.38E+04		2.63E+04
Ni		1.51E+02		4.13E+01		3.20E+01
P		8.14E+02	<	1.57E+01		1.24E+01
Pb		5.68E+01		1.32E+01		1.15E+01
Si		5.99E+01		62.6E+01		5.88E+01
Sn		2.51E+01		1.40E+00		1.37E+00
Sr		8.17E+01		8.36E-01		6.19E-01
Ti	<	1.11E+00	<	1.82E-01		1.82E-01
V	<	2.21E+00	<	2.73E-01		2.73E-01
Zn		9.35E+00		3.07E+00		2.74E+00
Zr		4.65E+00	<	3.64E-01		3.74E-01

Table 5.2. Characterization of barium precipitate wash with 0.01 M NaOH and deionized water

Sample ID		0.01 M NaOH wash-1		deionized water rinse-1		0.01 M NaOH wash-2
Cs-137 (µCi/mL)		2.30E-03		4.50E-05		4.61E-04
Co-60 (µCi/mL)	mda	7.67E-05	mda	7.86E-06	mda	1.27E-05
Eu-154 (µCi/mL)	mda	7.79E-05	mda	1.15E-05	mda	4.11E-05
Eu-155 (µCi/mL)	mda	9.62E-05	mda	1.68E-05	mda	7.11E-05
ICP-MS (mg/L)						
mass Tc-99		1.15E-01		5.24E-03		1.41E-02
massTh-232,		2.39E-02	<	9.42E-03	<	9.42E-03
mass U-233	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass U-235	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass U-236	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Np-237	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Pu/U-238	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Pu-239	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Pu-240	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Am/Pu-241	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Am-243	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Cm-245	<	9.42E-03	<	9.42E-03	<	9.42E-03
K (AA), mg/L		Nm		nm		nm
IC (mg/L)						
NO_3		6.88E+03		3.13E+02		1.385E+03
NO_2		1.41E+03		3.50E+01		2.49E+02
PO_4		3.80E+01		1.00E+01		1.90E+01
SO_4		3.40E+01		5.00E+00		1.10E+01

Oxalate		5.0E+01		6.00E+00		1.60E+01
Formate		2.23E+02		7.00E+00		3.8E+01
Cl-		1.70E+01		1.00E+00		8.00e+00
F-		1.30E+01		7.00E+00		8.00E+00
ICP-ES (mg/L)						
Al		2.35E+02		6.04E+00		3.86E+01
B		9.81E-01		1.05E-01		2.63E-01
Ba		1.12E+02		3.77E+01		5.39E+01
Ca		6.38E+00		8.92E-01		9.76E-01
Cd		1.01E+00		9.90E-02		1.77E-01
Co		6.68E-01		9.60E-02		8.30E-02
Cr		8.45E-01		8.90E-02		1.53E-01
Cu		5.79E-01		4.20E-02		7.50E-02
Fe		5.19E-01		4.60E-02		4.20E-02
La		1.25E+00		1.37E-01	<	1.10E-01
Li		4.01E-01		3.60E-02		2.90E-02
Mg		1.10E-01		2.60E-02		1.50E-02
Mn	<	9.1E-02	<	1.00E-02	<	1.00E-02
Mo		1.36E+00		1.01E-01		3.34E-01
Na		4.83E+03		2.43E+02		1.13E+03
Ni		6.09E+00		2.56E-01		9.37E-01
P		3.06E+00	<	9.98E-01		5.84E-01
Pb		5.99E+00		4.65E-01		6.15E-01
Si		4.93E+00		1.18E+00		2.09E+00
Sn		2.12E+00		2.20E-01		2.45E-01
Sr		2.31E-01		4.60E-02		4.80E-02
Ti		4.6E-01	<	3.70E-02		2.80E-02
V		7.02E-01	<	6.10E-02		5.50E-02
Zn		3.86E-01		3.80E-02		1.01E-01
Zr		7.61E-01		6.70E-02		6.10E-02

Table 5.3. Characterization of barium precipitate acid wash and accompanying water solutions

Sample ID		0.5 M HNO3 wash-1		deionized water rinse-1		1.0 M HNO3 wash-2
Cs-137 (µCi/mL)		4.60E-05	<	1.42E-05		6.94E-05
Co-60 (µCi/mL)		1.84E-05		1.48E-04		1.27E-05
Eu-154 (µCi/mL)		7.21E-05		2.35E-05		1.59E-04
Eu-155 (µCi/mL)		1.31E-04		4.00E-05		2.01E-04
ICP-MS (mg/L)						
mass Tc-99		1.10E-02		3.19E-03		1.64E-02
massTh-232,		1.08E-02	<	9.42E-03		1.97E-02
mass U-233	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass U-235	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass U-236	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Np-237	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Pu/U-238	<	9.42E-03	<	9.42E-03	<	9.42E-03

mass Pu-239	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Pu-240	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Am/Pu-241	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Am-243	<	9.42E-03	<	9.42E-03	<	9.42E-03
mass Cm-245	<	9.42E-03	<	9.42E-03	<	9.42E-03
K (AA), mg/L		nm		nm		nm
IC (mg/L)						
NO_3		5.49E+03		4.59E+03		2.90E+04
NO_2		9.00E+00		9.00E+00		6.30E+01
PO_4		2.10+01		2.10E+01		1.45E+01
SO_4		2.00E+00		2.00E+00		4.00E+00
Oxalate		9.0E+00		9.00E+00		2.60E+01
Formate		3.00E+00		3.00E+00		1.70E+01
Cl-	<	2.00E+00	<	2.00E+00		4.00E+00
F-	<	2.00E+00	<	2.00E+00		< 2.00E+00
ICP-ES (mg/L)						
Al		3.21E-01		2.40E-01		6.41E-01
B		5.07E-01		1.37E-01		3.45E-01
Ba		2.62E+04		4.72E+03		3.14E+04
Ca		5.64E+00		3.54E+00		1.50E+01
Cd		5.46E-01		1.69E-01		6.97E-01
Co		9.97E+00		1.87E+00		1.19E+01
Cr		2.35E-01		1.23E-01		4.11E-01
Cu		7.50E-02		3.20E-02		9.10E-02
Fe		8.00E-02		3.80E-02		1.09E-01
La		1.86E+00		4.92E-01		2.23E+00
Li		3.70E-02		3.00E-02		4.30E-02
Mg		1.60E-02		1.40E-02		2.0E-02
Mn		3.90E-02		1.20E-02		7.60E-02
Mo		1.14E-01		6.90E-02		1.03E-01
Na		9.58E+02		1.22E+02		7.37E+02
Ni		1.56E+00		3.95E-01		1.77E+00
P		1.41E+01		2.96E+01		2.50E+01
Pb		2.94E+00		6.79E-01		3.13E+00
Si		4.35E+00		7.10E-01		2.42E+00
Sn		5.69E-01		2.03E-01		4.46E-01
Sr		1.91E+01		4.42E+00		2.62E+01
Ti	<	2.00E-02	<	2.40E-02		2.70E-02
V		1.15E-01	<	6.90E-02		1.57E-01
Zn		1.03E-01		3.40E-02		8.80E-02
Zr		4.30E-02		5.10E-02		6.00E-02

Table 5.4. Analysis of alpha emitting radioisotopes in filtrate and wash solutions

Precipitate solurion	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)	Am-241 (dpm/mL)	Cm-244 (dpm/mL)
Ba precipitate filtrate	1.47E+02	3.51E+02	3.22E+02	2.01E+02
Composited filtrate product*	5.10E+01	1.53E+02	1.82E+02	9.60E+01
0.01M NaOH wash	8.71E+01	4.37E+02	6.91E+02	6.42E+01
Post NaOH water rinse	3.97E+02	6.37E+02	< 1.46E+02	1.48E+01
0.5 M nitric acid wash	4.24E+02	1.51E+02	5.46E+02	6.72E+02
Post acid water rinse	1.85E+01	5.74E+01	< 1.34E+02	6.61E+01

- product = composite of AN-102 filtrate and 0.01 M NaOH and water washes

Table 5.5. Particle size analysis of barium precipitate cake

Measurement	initial slurry solution	Post NaOH wash damp solids	Post acid wash damp solids	Final solid product (damp)
mean	29.88	17.21	22.62	5.25
median	28.98	14.61	21.85	1.39
20%	17.28	6.92	9.57	2.22
50%	28.98	14.61	21.85	1.39
80%	41.79	27.47	35.09	8.06

6.0 Bench Scale Precipitation and Evaporation of an Envelope B Simulant

6.1 Introduction

This section will discuss the bench scale sulfate precipitation and evaporation tests conducted using a simulant of tank 241-AZ-101. The principle objectives of this task are to provide the following information on the behavior of LAW solutions, following sulfate removal, during evaporation:

- Composition of the following solutions generated during the experiment

  - Initial Simulant prior to precipitation

  - Slurries generated prior to evaporation

  - LAW Filtrates and Wash solutions generated during filtration

  - Precipitates after washing

- Slurry Settling Rate and Physical Properties

- Precipitation Reaction Rate

- Bulk solubility of the Evaporator feed (AZ101 simulant following sulfate removal)

- Major precipitating species of the Evaporator feed

- Expected evaporator operating parameters (temperature, pressure)

- Extent of foaming and scaling during the evaporation

The composition of the evaporator concentrate and condensate was not completed since the task was terminated after the barium sulfate removal process was deleted from the RPP-WTP project.

6.2 Experimental

The baseline composition of the untreated AZ-101 (Envelope B) simulant was previously approved by RPP.[1, 2] The simulant was based upon Hanford tank 241-AZ101. The pre-fix "241" is common to all Hanford underground storage tanks and is not used further in this report. The sodium molarity of the simulant was designed to be approximately 4.74 M Na. Sulfate was added to match the concentration level (17670 mg/L @ 4.74 M Na) in the AZ101 tank. This corresponds to a sulfite concentration in the glass of approximately 1.148 wt. % SO_3 at 10 wt. %

Na$_2$O. Therefore, sulfate must be removed from this waste stream or the waste loading must be decreased below the solubility of sulfite in the LAW glass (0.2 wt. %).

Table 6.1 - Basis for the B Envelope Approved Simulant

Component	Moles/Liter	mg/Liter
Aluminum	3.95E-01	10670
Ammonium	1.84E-02	313
Cesium	2.81E-04	37
Chromium	1.40E-02	730
Potassium	1.18E-01	4624
Sodium	4.74E+00	108990
Zirconium	3.37E-05	3.1
Chloride	5.63E-03	200
Fluoride	9.54E-02	1813
Nitrate	1.22E+00	75632
Nitrite	1.41E+00	65063
Phosphate	1.58E-02	1503
Sulfate	1.84E-01	17670

Table 6.2 - Composition of Envelope B Simulant Based on Tank AZ-101

Compounds	Formula	Grams/Liter
Ammonium Nitrate	NH_4NO_3	1.470
Cesium Nitrate	$CsNO_3$	0.055
Zirconyl Nitrate	$ZrO(NO_3)_2 \bullet xH_2O$, x~1	0.008
Potassium Nitrate	KNO_3	11.956
Sodium Chloride	$NaCl$	0.329
Sodium Fluoride	NaF	4.008
Sodium Chromate	Na_2CrO_4	2.274
Sodium Sulfate	Na_2SO_4	26.128
Aluminum Trihydroxide	$Al(OH)_3$	30.839
Sodium Hydroxide	$NaOH$	37.205
Sodium Phosphate	$Na_3PO_4 \bullet 12H_2O$	6.015
Sodium Carbonate	Na_2CO_3	40.757
Sodium Nitrate	$NaNO_3$	92.027
Sodium Nitrite	$NaNO_2$	97.583
Water	H_2O	845.93

The simulant used in the bench-scale evaporator experiments was prepared in a 35 liter batch and stored for 24 hours before filtering through a Whitman 0.2 μm filter. All chemicals used were of reagent grade and deionized water was used to prepare the solutions. The filtered AZ101 simulant was analyzed according to Table 6.3.

Table 6.3 - Analytical Requirements for AZ101 Simulant, Filtrates and Sulfate Precipitate

Analyte	Precipitate Solids Minimum Reportable Quantity mg/g	AZ101 Simulant/Filtrate Minimum Reportable Quantity mg/ml	Analysis Method
**Analytical Requirements for Sulfate Precipitate, Filtrate and Simulant**			
Al	3.3E+02	7.5E+01	Acid Digestion (*and* KOH Fusion for solids samples) followed by: ICP-AES
Ba	6.0E+02	1.0E+01	
Ca	1.8E+02	1.5E+02	
Cr	1.2E+02	1.0E+00	
Fe	1.4E+02	1.5E+02	
K	1.5E+03	2.0E+02	
La	6.0E+01	3.5E+01	
Mg	5.4E+02	1.5E+02	
Mn	3.0E+02	1.5E+02	
Nd	7.7E+01	Not required	
Na	1.5E+02	7.5E+01	
Ni	1.6E+02	3.0E+01	
P	6.0E+03	3.3E+02	
Pb	6.0E+02	1.0E+00	
Si	3.0E+03	1.7E+02	
U	6.0E+02	6.0E+02	
Zn	6.0E+00	1.65E+01	
Zr	6.0E+02	N/A	
TOC	6.0E+01	1.5E+03	TOC
TIC	3.0E+01	1.5E+02	TIC
Cl	2.3E+02	2.5E+01	IC
F	7.5E+03	1.5E+02	
NO_3	4.5E+02	3.0E+03	
SO_4	1.2E+03 (as S)	2.3E+03	
PO_4	6.0E+02 (as P)	2.5E+03	
Wt. % Total Solids / Soluble Solids / Insoluble Solids	N/A	0.25 wt. %	Gravimetry
Density	N/A	0.9 gm/ml	

A 0.27 M solution of $Ba(NO_3)_2$ was made up and used as the reagent sulfate precipitation. Approximately 282.3 g of $Ba(NO_3)_2$ was added to 3937 g water to yield approximately 4000 ml of 0.27 M $Ba(NO_3)_2$ solution.

Approximately 4000 ml of 0.45 M HNO3 and 0.01 M NaOH wash solutions were also formulated. These solutions were used to wash the barium sulfate precipitate.

AZ-101 Simulant Sulfate Precipitation by Addition of Barium Nitrate Solution

A procedure, developed by Hay and Coleman, was used to remove the sulfate from the AZ101 simulant. Johnson documented the procedure in [3]. The experimental procedure and analytical data taken during the experiment are described below:

1. Add sufficient 0.25 to 0.30M barium nitrate solution to the 3 liters of the simulated AZ-101 solution to achieve 1.3 moles of Ba per mole of Sulfate. The solution should be constantly stirred during this addition. The reaction was conducted in an 8-L vessel that was stirred with a variable speed agitator. The barium nitrate solution was pumped into the vessel through a subsurface addition tube.

2. After adding the barium nitrate solution, the settling rate of the barium precipitate was measured (cm per minute) over one minute interval for a total of one hour.

3. The settled barium precipitate was resuspended. Samples of the slurry were obtained and analyzed for weight percent insoluble solids, viscosity versus shear rate, density, and particle size distribution.

4. While constantly stirring the simulant to suspend the precipitate, the barium precipitate slurry was sampled at intervals of 2, 4, 8, and 24-hours to determine the reaction rate. The samples were filtered analyzed for the constituents listed in Table 6.4

Table 6.4 - Analytical Requirements for Sulfate Precipitate Filtrate during Reaction Rate Test

Analytical Requirements for Sulfate Precipitate Filtrate During Reaction Rate Test		
Analyte	Filtrate Minimum Reportable Quantity μg/ml	Analysis Method
Cl	2.5E+01	
F	1.5E+02	
NO_3	3.0E+03	IC
SO_4	2.3E+03	
PO_4	2.5E+03	
Density	0.9 gm/ml	

5. 24-hours after the addition of barium nitrate, the slurry was filtered using a 0.45 μ filter. The filter flux rate was measured. The AZ101 filtrate was analyzed to determine pH and the concentration of analytes listed in Table 6.3. A sub-sample of the barium precipitate was dried to a constant weight using a Microwave, weighed, and the wt. % water in the original damp precipitate was determined.

6. The damp barium precipitate was washed and filtered (0.45-μm filter element) as follows:

   a. Twice with 2:1 volume ratio of 0.01 ±0.005M NaOH solution, combining the two dilute caustic wash solutions.

   b. Twice with 2:1 volume ratio of 0.45 ± 0.05M HNO_3 solution, combining the two nitric acid solutions.

   c. Twice with 3:1 volume ratio of demineralized water, combining the water wash solutions.

   d. The dilute caustic wash, nitric acid, and water wash solutions were analyzed to determine pH and the concentration of analytes listed in Table 6.3

   e. The caustic wash solutions were combined with the AZ101 filtrate (step 5), placed in a sealed container, and examined for precipitation at intervals of about 24-hours for the time period before conducting the evaporation test.

   f. A sub-sample of the washed barium precipitate was dried to a constant weight using a Microwave, weighed (± 0.1gm), and the wt. % water in the original damp precipitate determined.

   g. A sub-sample of the washed barium precipitate was tested to determine if this solid exhibits toxicity characteristics using the Toxicity Characteristic Leaching Procedure (TCLP, per 40 CFR Part 261).

Evaporator Equipment and Procedures

Figure 6.1 shows the sketch of the bench-scale evaporator unit. The evaporator pot was designed based upon a natural-circulation calandria (thermosiphon reboiler). Thermosiphon evaporators operate by density differences between the liquid entering the heat exchanger and the two-phase vapor-liquid mixture that is generated in and exits the heat exchanger.[4] The design of the experimental apparatus was also based upon the experimental design detailed in the reference.[5] The operating pressure of the RPP-WTP evaporator coupled with the constraints of the laboratory hood dictated use of this design

The evaporator, condenser, and concentrate receipt tanks were constructed of sodium borosilicate glass tubing (100 mm). These vessels have a working volume of approximately 1 to 1.8 L (nominal 1.5 L for the evaporator). Decals were affixed to the outer walls of each vessel to provide an indication of level. The vessels were calibrated with deionized water prior to initiation of any experimental work. Fresh evaporator feed was added to and withdrawn from the evaporator using peristaltic pumps. Peristaltic pumps were also used to withdraw concentrate and condensate from the system.
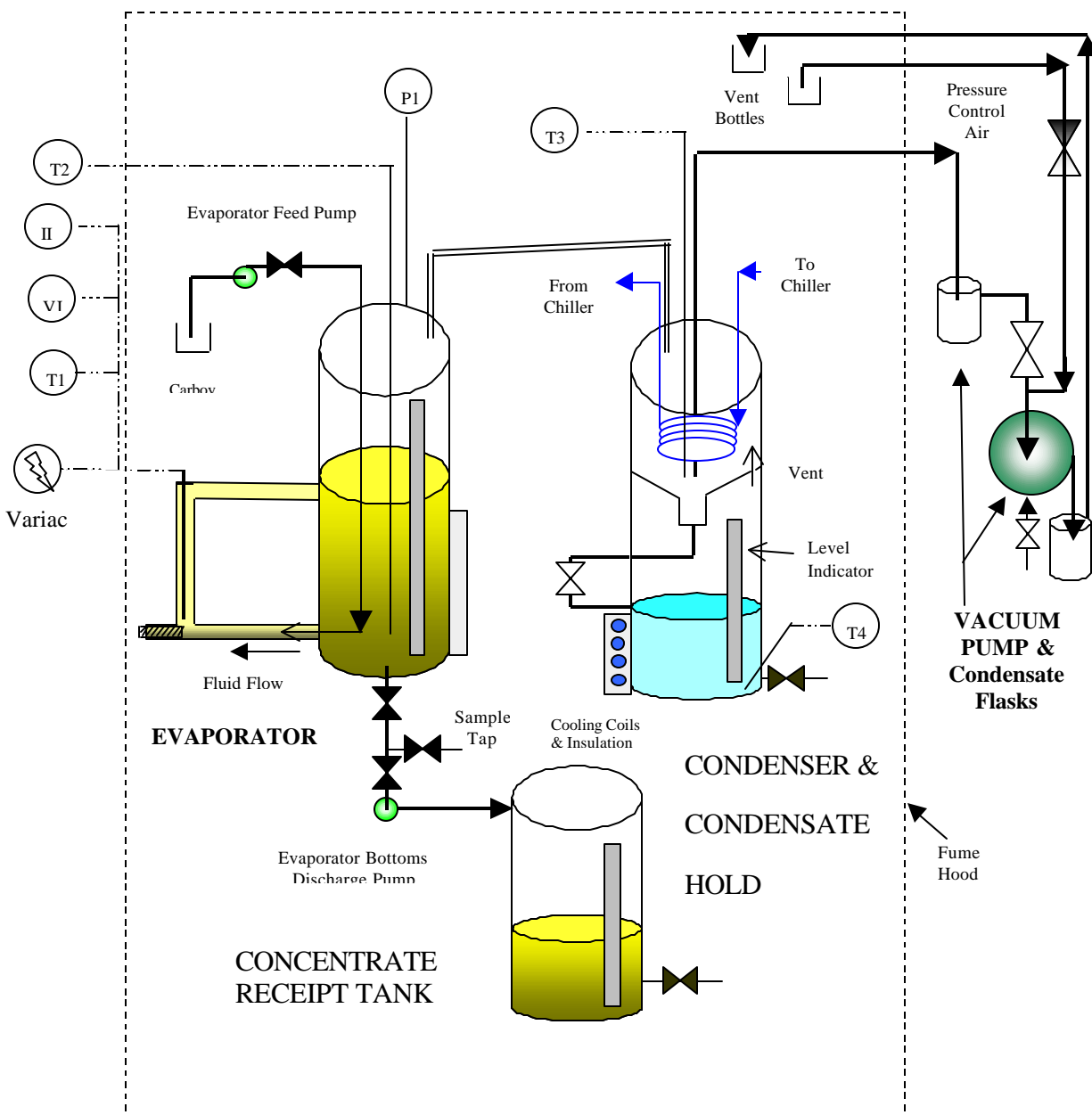
Figure 6.1 – Bench Scale Evaporator at SRTC

Norprene ® (corrosion resistant, full vacuum rated) tubing was used on all liquid pumping systems. The evaporator was heated using corrosion and oxidation resistant Incoloy ® 1000 W resistant heater. The heater had an internal thermocouple that gives a reasonable approximation of the heater surface temperature. The temperature difference between the heater surface and the evaporator pot gave a secondary indication of scaling on the heat transfer surface. The primary indication of scaling was visual coupled with the analyses by the scanning electron microscope and/or the X-ray diffraction instruments. The following system parameters were measured during each experiment (refer to Figure 6.1):

- Heater Voltage and Current (VI & II)

- Heater Surface Temperature (T1)

- Evaporator Temperature and Pressure (T2, P1)

- Condenser Temperature (T3)

- Condensate Hold Tank Temperature (T4)

- Condenser Chiller Temperature

- Condensate Hold Tank Temperature

- Vessel Volumes

- Evaporator Feed and Discharge Flow rates

System vacuum was maintained using an oil free PTFE diaphragm vacuum pump that was capable of an ultimate vacuum of 9 torr. The vacuum pump was connected to the system with 304-L stainless steel tubing.

System air in-leakage was measured before the experiment by conducting a standard air in-leakage (drop) test for vacuum systems.[6] The test is based on the fact that air leaks into the system at a constant rate as long as the pressure in the system is less than 0.53 times atmospheric pressure ($\approx$ 400 torr). The test was run with the system empty but with all rotating equipment and other moving equipment in operation to duplicate the leakage through seals. An accurate measurement of the total system volume and the pressure rise over measured time duration is all that is required to estimate the air in-leakage in any system. Since the system volume was measured using deionized water for the bench-scale evaporator, air in-leakage could easily be determined.

The evaporator was run in a semi-batch mode. The bench-scale evaporator was initially charged with approximately 1.5 L of a combined mixture of barium precipitate (AZ101) filtrate and caustic wash (evaporator feed) solution. Additional evaporator feed was added to maintain the

evaporator level at a constant value. The evaporator feed was added until the evaporator concentrate became saturated and solids formed in the evaporator. Samples were taken at periodic intervals and analyzed for % total/insoluble/soluble solids and density. If insoluble solids were present in the samples, the sample was filtered and the filter paper was analyzed by X-Ray Diffraction to determine type of crystal formed.

The system pressure was maintained at a constant value of 64 torr (27.4 in. Hg vacuum gauge). The operating pressure was selected based upon previous experience with evaporating simulated Hanford wastes.[7, 8] The condenser temperature was maintained at 40°C which is the design basis temperature for the RPP-WTP pretreated LAW evaporator. Since scaling could be an issue in evaporation processes, the heat flux through the heated rod was maintained at 9.0 W/cm^2. This is a conservative value with respect to scaling when compared to the RPP LAW Melter Feed Evaporator design basis (7.9 W/cm^2).

The test specification for the task identifies the data reporting and data quality requirements.[3]

6.3   Results and Discussion

Table 6.5 shows the planned vs. the measured composition of the AN105 simulant used for the evaporation experiments. The % difference between the predicted values and the analytical measurements is shown for comparison. The measured density and % total solids values compare favorably with the planned values. The simulant was filtered and samples were submitted for analysis. Approximately 0.6 % of the total salts added were filtered from the simulant.

Analytical values compared favorably with planned values except for Al, Zr, TIC, TOC, Cl, F and PO_4. The low aluminum result was traced to the aluminum trihydroxide that was used. The aluminum source was only 80% pure due to absorbed water; therefore, the aluminum measured was actually very close to the amount added. The high TIC result was probably due to carbon dioxide absorption, leading to the production of carbonate. The low F and PO_4 may be due to the formation and subsequent precipitation of the double salt, sodium fluoride diphosphate hydrate, $Na_7F(PO_4)_2 \cdot 19H_2O$. This simulant was found to be nearly saturated (80%) with $Na_7F(PO_4)_2 \cdot 19H_2O$. Low chloride values are unexpected and are probably due to analytical error. Organic compounds were not added to the simulant. High TOC values are likely due to contamination from antifoams used in previous experiments, laboratory cleaning soap, or phthalates from laboratory tubing or plastic storage containers. Laboratory contamination of the sample with organics could offer one explanation for the organic levels found in the simulant. Low Zr values were also found in [8] and might be due to the presence of trace levels of complexants in the actual AZ-101, thus allowing for a higher solubility of trace metals in the actual waste than could be achieved in the simulant.

Table 6.5 - Envelope B AZ101 Simulant – Planned vs. Measured

Analyte	AZ101 SIMULANT Planned, mg/L		AZ101 SIMULANT Measured, mg/L (After Filtration)	% Difference
Al	10670		8190	26.3%
Ba	NA	<	0.1	
Ca	NA		3.5	
Cr	730		735	-0.7%
Fe	NA		0.16	
K	4624		4850	-4.8%
La	NA	<	0.1	
Mg	NA	<	0.084	
Mn	NA	<	0.009	
Nd	NA	<	0.25	
Na	108990		111711	-2.5%
Ni	NA	<	0.1	
P	490		534	-8.6%
Pb	NA	<	0.7	
Si	NA		5.6	
Zn	NA		0.7	
Zr	3.1		0.7	126.3%
TOC	NA		789	
TIC	4620		7294	-44.9%
Cl	200		308	-42.5%
F	1813		497	113.9%
NO3	75632		74128	2.0%
SO4	17670		16647	6.0%
PO4	1503		1320	13.0%
Wt. % Total Solids	29.22		28.24	3.5
Density, mg/L	1.23		1.24	-0.9%

AZ-101 Simulant Sulfate Precipitation by Addition of Barium Nitrate Solution

The barium nitrate solution was added to the AZ101 simulant in a well-agitated vessel. A peristaltic pump was used to add the barium nitrate solution at a rate of 10 ml/min. The 0.27 M barium nitrate solution was added to achieve a molar ratio of 1.3 moles of Ba per mole SO_4 (0.789 g $Ba(NO_3)_2$ solution / g AZ101 simulant) in the combined mixture. The reaction is immediate. A settling test was also conducted after the barium nitrate addition was completed. Appendix 4 shows pictures of these settling tests.

Settling Rate - Barium Sulfate Precipitate
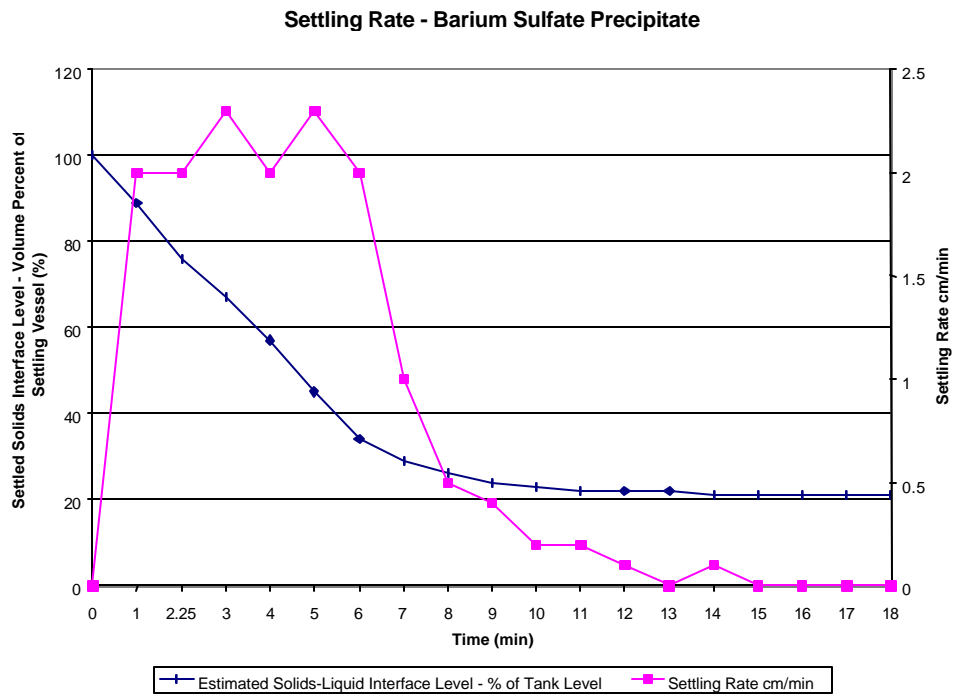
Figure 6.2 - Settling Rate Test - Settling Rate and Barium Precipitate Interface Level as a Function of Time

Table 6.6 - Physical Properties of Barium Precipitate Slurry

PROPERTY	VALUE	ANALYTICAL TECHNIQUE
% Total Solids	19.1	Gravimetry
% Soluble Solids	14.9	Gravimetry
% Insoluble Solids	4.2	Gravimetry
Density, g/ml	1.146	Pycnometer
Viscosity, cp	Newtonian, 1.8	Concentric Cyclinder – Haake M5 NV Sensor

Table 6.7 - Summary Particle Size Analysis for Barium Precipitate

MEASUREMENT	DESCRIPTION	VALUE (MICRON)
Mv	Mean Diameter based on Particle Volume	9.515
Mn	Mean Diameter of the Number Distribution	1.745
Ma	Mean Diameter of the Area Distribution	6.346
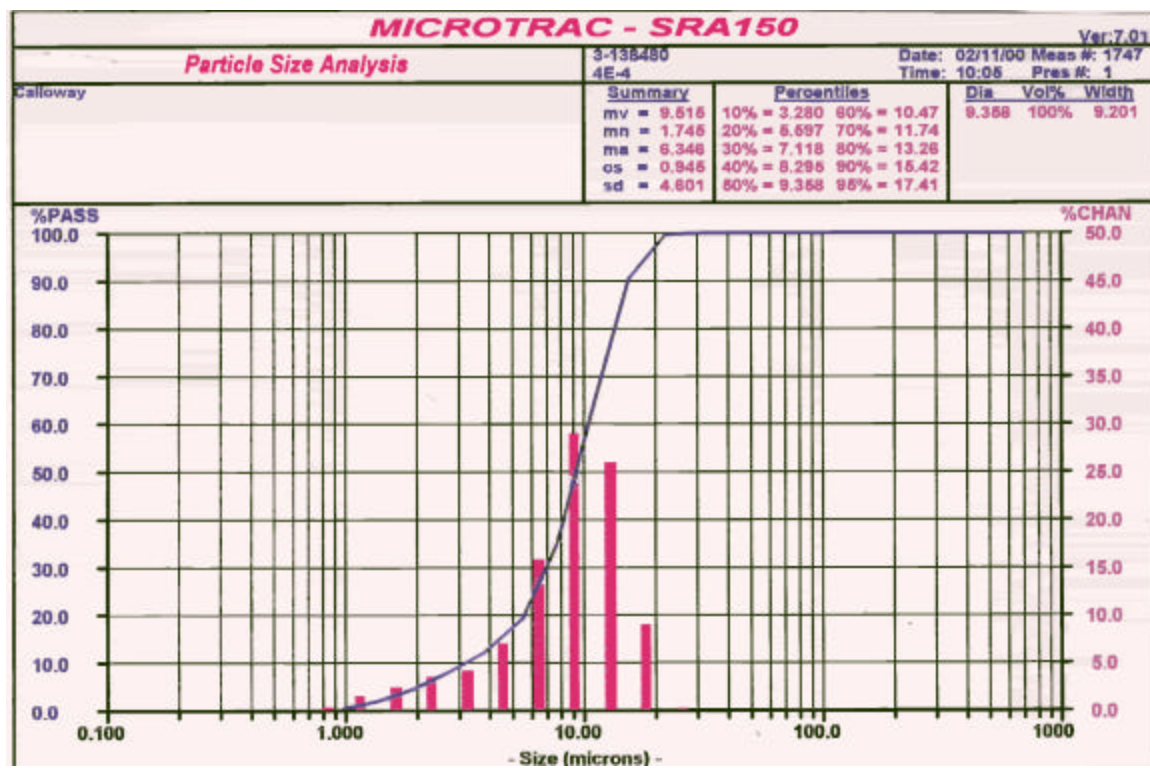
Figure 6.3 - Detailed Particle Size Analysis of Barium Precipitate

Table 6.8 - Barium Precipitate Filtrate during Reaction Rate Test

	SAMPLE TIME (HOURS AFTER ADDITION)				
	0	2	4	8	24
Analyte					
Cl, mg/L	221	215	224	225	225
F, mg/L	426	398	421	421	418
NO3, mg/L	58122	54649	58729	55343	59118
NO2, mg/L	33995	31560	35604	35998	35908
PO4, mg/L	637	615	648	654	682
SO4, mg/L	1146	1111	1188	1199	1148
AZ101 Simulant SO4 Concentration, mg/L	17670	17670	17670	17670	17670
SO4 Removal DF (AZ101 Simulant / Supernate)	15.4	15.9	14.9	14.7	15.4

A settling test was conducted after the barium nitrate addition was completed. The barium precipitate settles rapidly and can be characterized as a fast settling heterogeneous slurry. The calculated settling rate (cm/min) is shown in Figure 6.2. The barium precipitate settled to approximately 20 volume % at a settling rate of approximately 2 cm/min.

The barium precipitate was resuspended and characterized for various physical properties as shown in Table 6.6, Table 6.7, and Figure 6.3. As expected, the barium precipitate is a Newtonian fluid.

The barium precipitate slurry was resuspended and samples were taken, filtered and the supernate characterized to determine if the barium precipitation reaction was completed. Analysis of Figure 6.2 and Table 6.8 indicates that the barium precipitation reaction is rapid and comes to equilibrium within one hour after the addition of barium nitrate.

The entire batch of barium precipitate slurry was filtered using a vacuum filtration apparatus that was operated at an absolute vacuum of 28 torr. An average filter flux of 106 ml/min (85.9 m^3/[m^2·day]) was obtained using a 0.45 μ filter. Filter flux data was calculated from the following equation:

Filter flux = Volume flow / [Filter surface area · day]

The filter flux data obtained from beaker tests should not be directly compared to filter fluxes obtained using a cross flow filter. Filter flux data developed from dead-end filters should only be used to beakers compared filterability within a dead-end filtration data base. The filtrate was characterized according to Table 6.3 and the results are reported in Table 6.9. The RPP-WTP

design was changed to delete the sulfate removal process before a method to dissolve and analyze the barium precipitate could be developed. The % total solids for the filtered barium precipitate was measured to be 64.4 %.

The damp barium precipitate was washed twice in an agitated vessel with a 2:1 volume ratio of 0.01 M NaOH solution and the dilute caustic washes were combined with the barium precipitate filtrate. After the initial caustic wash, the precipitate was washed twice with a 2:1 volume ratio of 0.45 M HNO_3. The precipitate was then washed with a 3:1 volume ratio of demineralized water. The wash solutions were analyzed according to Table 6.3 and the results are presented in Table 6.9.

The washed barium precipitate was tested to determine if the solid exhibits toxicity characteristics using the Toxicity Characteristic Leaching Procedure (TCLP, per 40 CFR Part 261). The sample tested positive for barium (>100 mg/L in the leachate) indicating that further treatment would be required before a permanent disposal route could be devised. The results are presented in Table 6.10.

Table 6.9 - Barium Precipitate Filtrate, Wash Solution and Combined Barium Precipitate/Caustic Wash Solution Analysis

ANALYTE		BARIUM PRECIPITATE FILTRATE, AVERAGE CONCENTRATION	STANDARD DEVIATION FOR BARIUM PRECIPITATE FILTRATE		CAUSTIC WASH		ACID WASH		DEMINERLIZED WATER WASH		COMBINED BARIUM PRECIPITATE FILTRATE AND CAUSTIC WASH (EVAPORATOR FEED)
Al		4435	12.91		517		32	<	0.24		3792
Ba		2	0.08		1.1		19266		2848		1.9
Ca		0.12	0.01		0.07		12.3		1.38		0.08
Cr		29	0.52		2.88		2.4	<	0.10		24
Fe		0.19	0.04	<	0.05	<	0	<	0.05		0.15
K		2570	14.14		373		56		4.2		2172
La	<	0.100	0.00	<	0.1	<	0.10	<	0.10	<	0.10
Mg	<	0.084	0.00	<	0.08		0.92		0.10	<	0.08
Mn	<	0.009	0.01	<	0.009		0.37		0.05	<	0.009
Nd	<	0.25	0.00		NR		NR		NR		NR
Na		60715	1096		7413		746		53		50153
Ni	<	0.1	0.00	<	0.1	<	0.1	<	0.10	<	0.1
P		222	2.06		29		62	<	0.7		188
Pb	<	0.7	0.00	<	0.7	<	0.7	<	0.7	<	0.7
Si		3.4	0.16		0.9		0.5		0.2		2.8
Zn		0.9	0.05	<	0.37	<	0.37	<	0.4		0.77
Zr		0.1	0.01	<	0.048	<	0.048	<	0.0		0.08
TOC		395	139		80		39		41		307
TIC		4030	859		731	<	1		5		2530
Cl		88	2.1		129	<	20	<	20		NM
F		418	6.70		87		11	<	20		NM
NO3		43877	1117		6878		23565		2442		NM
SO4		1019	26		231	<	50	<	50		NM
PO4		561	15		234		217	<	100		NM
Wt. % Total Solids		17.85	0.00		2.48		4.84		0.78		13.8
Density, mg/L		1.128	0.0005		1.01		1.00		0.997		1.110

NR/NA/NM – Not Reported/Not Applicable/Not Measured

Table 6.10 - TCLP Results for Washed Barium Precipitate

ANALYTE	TCLP RESULTS FOR WASHED BARIUM PRECIPITATE, MG/L
Ba	**341**
Cd	<0.005
Cr	0.25
Pb	<0.05
Ag	<0.03

Bench Scale Evaporation

The bench-scale evaporator was initially charged with the combined mixture of barium precipitate (AZ101) filtrate and caustic wash (evaporator feed) and heated at a constant heat flux of 9.15 W/cm^2 of boiling surface. Once boiling was initiated, the cooling water to the condenser was adjusted to maintain the vapor temperature in the condenser at the design basis value of 40 °C. The pressure was set at 64 torr. Samples were taken periodically and analyzed for solids content and density. The evaporator feed boiled at a temperature of 50 °C. A boiling point rise of approximately 5 °C was experienced during the evaporation. No foaming or scaling of the heat transfer surface was observed during the experiment. The measured vapor flux was 0.47 kg/min/m^2, which is approximately 1/12th of the design basis vapor flux (5.66 kg/min/m^2).[9] While an indication of no foaming during a small-scale experiment is a positive result, a definitive determination of foaming can not be made without achieving the design basis vapor flux. No antifoam was added during the experiment.

Samples were pulled periodically to track the concentration of the evaporator product. The samples were allowed to cool to ambient conditions and analyzed for solids content and density. If solids were present, the samples were filtered and the dry solids were analyzed by x-ray diffraction. Figure 6.4 shows the evaporator density and concentration during the evaporation. The pretreated simulant was fed into the evaporator at a density of 1.11 g/ml and was concentrated to a density > 1.4 g/ml.
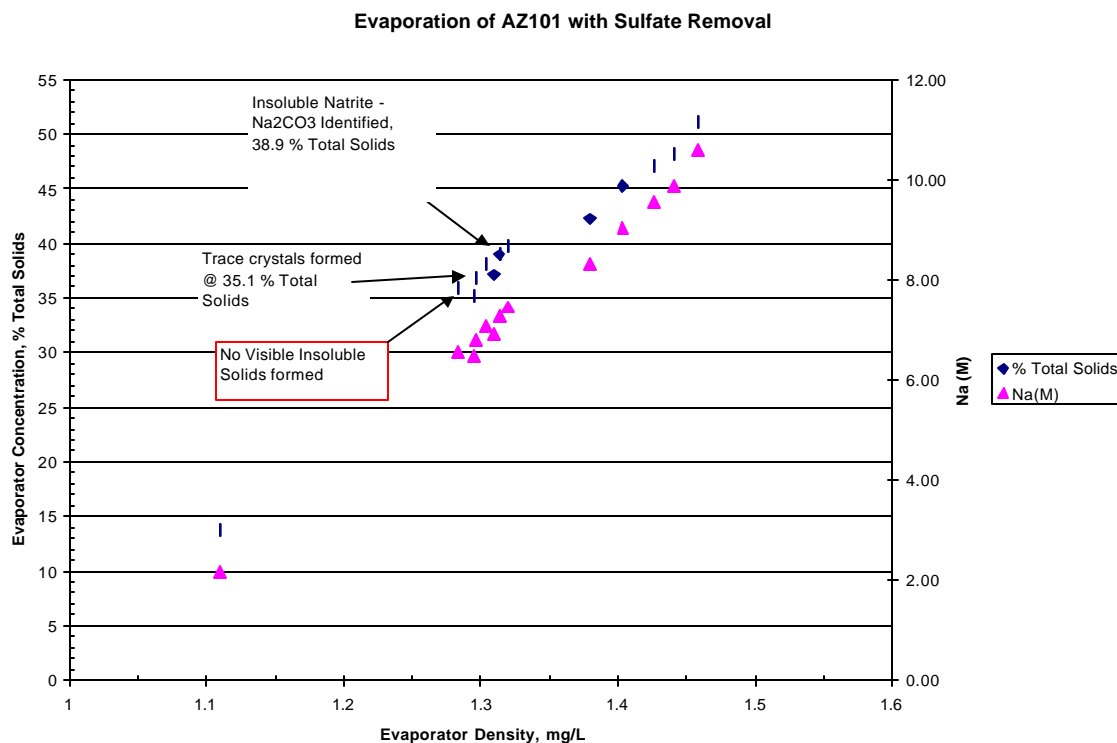
Figure 6.4 - Evaporation of AZ101 Simulant treated to Remove Sulfate – Natrite Identified at a Concentration of 1.31 g/ml and 38.9 % Total Solids

Figure 6.5 shows the x-ray diffraction (XRD) scans for two of the samples taken during the experiment. The two XRD scans corresponds to the points, 35.1 and 38.9 wt. % total solids in Figure 6.4. Trace quantities of insoluble solids began to form at a concentration of 35.1 % total solids. The insoluble solids formed at 35.1 wt. % were Sodium Nitrate, Sodium Nitrite, Trona ($Na_3H(CO_3)_2 \cdot 2H_2O$) and Sodium Aluminum Silicate Bis(2-Hydroxyethyl)Dimethylammonium. Sodium Aluminum Silicate Bis(2-Hydroxyethyl)Dimethylammonium likely formed due to the presence of trace quantities of commercial soaps used to clean the experimental rigs. No organic compounds were added to the AZ101 simulant but TOC analysis indicates that some organic is present. Additionally, large quantities (1g/L) of antifoam were previously used in the experiment rig and could also be the source of the TOC contamination. These compounds were also identified in samples that did not have any visible solids. Therefore, it is likely these compounds were formed upon drying of the supernate and/or are present in only trace quantities as indicated (qualitatively) in the XRD scan for 35.1 wt. % total solids. The XRD scan for 38.9 wt. % is more pronounced and also shows the presence of Natrite (Na_2CO_3) for the first time. XRD scans for more dilute samples did not contain Natrite. All the XRD scans at higher evaporator concentration include Sodium Nitrate, Sodium Nitrite, Trona ($Na_3H(CO_3)_2 \cdot 2H_2O$), Sodium Aluminum Silicate Bis(2-Hydroxyethyl)Dimethylammonium, and Natrite (Na_2CO_3).
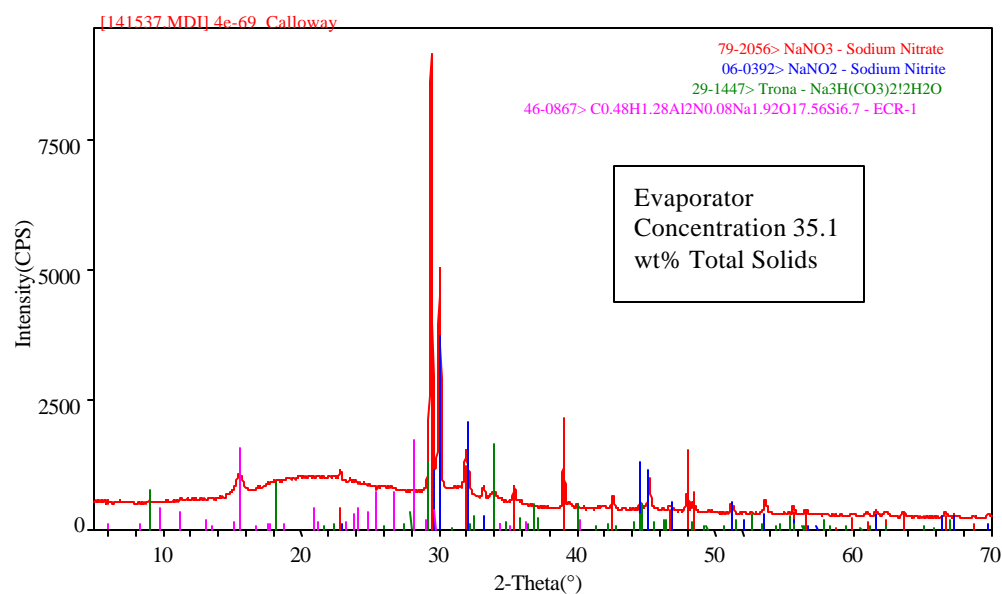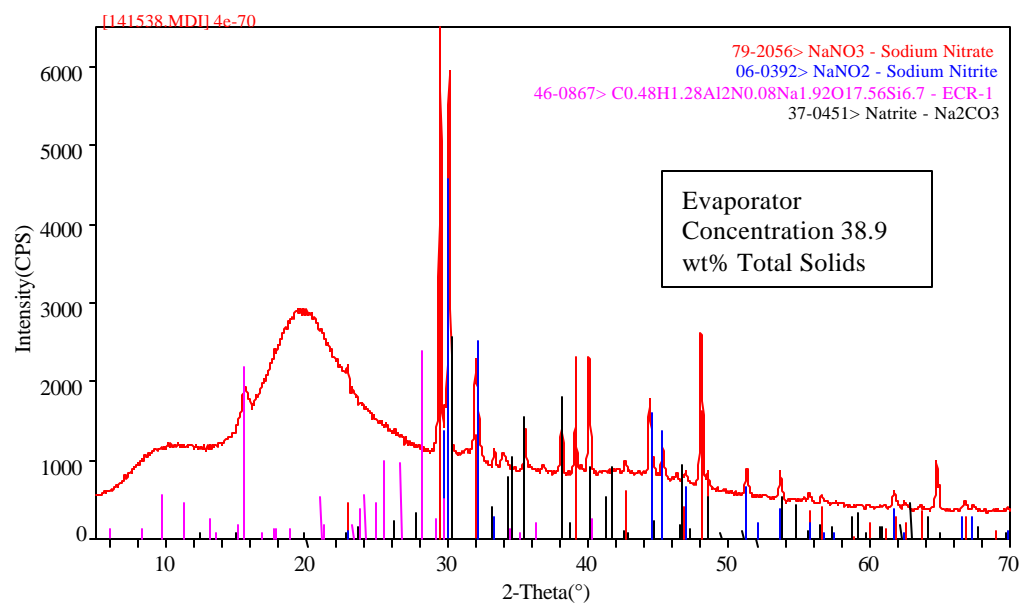
Figure 6.5 - X-Ray Diffraction for Insoluble Solids formed in Evaporator Samples Concentrated to 35.1 and 38.9 wt. % Total Solids

Therefore, it is likely that the major precipitating species for the AZ101 (sulfate removed) simulant is Natrite. The bulk solubility point (@ 20°C) for this simulant is approximately 38.9 wt. % total solids. This differs from previous experiments conducted with AZ101 simulant that did not include sulfate pretreatment.[8] Previous experiments determined that AZ101 simulant could not be evaporated beyond 4.74 M Na. Additionally, the double salt, $Na_7F(PO_4)_2 \cdot 19H_2O$ was found to be the major precipitating species.

6.4   Conclusions

The washed barium precipitate was tested to determine if the solid exhibits toxicity characteristics using the Toxicity Characteristic Leaching Procedure (TCLP, per 40 CFR Part 261). The sample tested positive for barium(>100 mg/L in the leachate) indicating that further treatment would be required before a permanent disposal route could be devised.

The major precipitating species for the AZ101 (sulfate removed) simulant is Natrite (Na_2CO_3). The bulk solubility point (@ 20°C) for this simulant is approximately 38.9 wt. % total solids.

6.5   References

1.   BNFL Letter No. 001696, TWRS-P Contract No. DE-AC06-96RL13308 – W375 – Approval of LAW Envelope A and B Simulants, Michael E. Johnson to Steven T. Wach, 2/16/99

2.   R. E. Eibling et. al., Hanford Waste Simulants Created to Support the Research and Development on the River Protection Project – Waste Treatment Plant, WSRC-TR-2000-00338, Westinghouse Savannah River Company, Draft 11/30/00.

3.   TSP-W375-99-00016, Test Specification for Separating Sulfate from Pretreated AN107, AZ102 and AN102 Solutions by Precipitation, Rev. 2 1/4/2000

4.   Minton, Paul E., Handbook of Evaporation Technology, Noyes Publications, Mill Rd. Park Ridge, NJ, Library of Congress 86-17978, 1986.

5.   Nash, C. A., Task Technical and Quality Assurance Plan for the CIF Bench Evaporator (U), WSRC-RP-98-00328 Rev. 1, Westinghouse Savannah River Company Aiken, SC, 9/18/98.

6.   Standards for Steam Jet Ejectors 3rd Edition, Heat Exchanger Institute 122 East 42nd St   New York, NY, 3rd Edition, 1956.

7.   T. B. Calloway, Jr., Evaporation of Hanford Envelope A Simulant (AN-105), WSRC-TR-2000-00300 Rev. 0, Westinghouse Savannah River Company, August 2000

8.   T. B. Calloway, Jr. et. al., Evaporation of Hanford Envelope B Simulant (AZ-101) Preliminary Report, BNF-003-98-0166 Rev. 1, Westinghouse Savannah River Company, 1/6/2000

9.   M. Washer, Evaporator Info, Email to H. Saito, BNFL Inc., Richland WA, 3/9/2000.

7.0 Low Temperature Crystallization and Non-Inorganic Precipitating Agents

7.1 Introduction

This section covers two methods that were tested: chilled crystallization, and two sulfate precipitants. Chilled crystallization was evaluated by cooling simulant samples (undiluted, diluted, or with additive) until significant solids formed, decanting the liquid phase, and analyzing both phases for sulfate content. Of the two precipitating agents investigated the 2-Amino Perimidine study consisted of treating two 100-mL portions of chromated Envelope B high-sulfate simulant, where the same 2-Amino Perimidine solid was used for both treatments through regeneration with 5 M NaOH. The current study presents sulfate removal data, impacts on other ions of importance, physical considerations for process scale-up, and items for further study.

The desired process will target sulfate without removing significant amounts of other waste components. Other components of the waste removed with the sulfate must be compatible with the Hanford Effluent Treatment Facility (ETF). Components of concern for the ETF include hazardous metals like chromium and lead. The desired process is to remove as little as possible of components that are intended for the low level waste melter such as nitrate and nitrite.

Background on 2-Amino Perimidine

2-Amino Perimidine (2-AP) is an alkaloid organic reagent (CAS # 28832-64-6) used in analytical wet chemistry to determine sulfate by precipitation. It was first shown to be effective for that task by Stephen.[1] A method of recycling the material was also provided because of the relative rarity and cost of the material at the time. The key property of the material is its low solubility in water when in the sulfate form. Stephen found the solubility of the 2-AP sulfate to be 20 mg/l.

2-AP is a solid (melting point 282 C for the hydrogen chloride form). It is susceptible to oxidation on contact with air. McClure gives a practical synthesis.[2] As an alkaloid it forms ion pairs preferentially with sulfate and hydrogen ion together.

Other aromatic amines have been studied elsewhere for sulfate precipitation. 4-Amino-4'-chlorodiphenyl and 4,4'-diaminobiphenyl are examples. The work was done with 2-AP alone here because it was taken as representative of this class of aromatic compounds, some of the other members having known carcinogenicity.[3, 4, 5]

Plans for the current study were to treat two 100-mL portions of simulant and to demonstrate the regeneration of the 2-AP after the first treatment. Figure 7.1 is a flowchart of the process and sample plan as performed. Note that a 100 ml portion of simulant contains 0.01 moles of sulfate, and that the 3 grams of 2-AP used is also 0.01 moles.

Background on Cobalt Complexes

Hexammine cobalt halides were studied by Mahr and Kraus to precipitate sulfate.[6] Werner complexes of ammine-coordinated cobalt were found to be promising reagents for sulfate precipitation as well.[7, 8] Since the Werner complexes are not available commercially and are synthesized with difficulty only cobalt hexammine trichloride was tested in the current work. It is sparingly soluble in water and was thus added as a solid to the simulant to be treated.

Background on Low-Temperature Crystallization

Crystallization is a commonly used unit operation for separation or purification of process streams. Removal of sodium carbonate from brine is achieved by reaction with carbon dioxide to form a less soluble sodium bicarbonate, which can be readily crystallized and separated from the stream. Another example is the separation of p-xylene from its ortho and meta isomers, where p-xylene is crystallized at the top of a column and flows downward as purified o- and m-xylene is produced on its way up the column.[9] Process equipment can vary from a simple stirred tank to a multi-phase column, with cooling being achieved by simple ambient cooling to use of heat exchangers. In the case of para and meta-xylene separation, para-xylene purities greater than 99% have been attained using low-temperature fractional crystallization.[10]

Herting[11] studied the removal of sodium nitrate using fractional crystallization of acidified Hanford tank wastes. In this case, evaporation rather than temperature was used to affect solubility of the target compound. About 80% of initial $NaNO_3$ in the feed was recovered as crystallized material in the testing of SY-101 tank waste. 72% of initial sulfate, an anion present in small quantities, was removed from the feed during crystallization of AW-101 waste while recovering 66% of the initial sodium nitrate. This report also cited the possibility of recovering sulfate from Hanford wastes as ammonium alum $(NH_4Al(SO_4)_2 \cdot 12\ H_2O)$. Dawson[12], in his study of solubilities of sodium sulfate and ammonium sulfate in water, showed that the sulfates can be separated from each other by subjecting solutions of certain concentrations to low temperatures.

For simplicity in this scoping study, samples of BNFL simulants containing sulfate were placed in vials and chilled in a cold bath using glycerin/water mixtures as the heat transfer medium. Solutions were chilled until roughly half of the sample was frozen, and the liquor was decanted/extracted from the vial.

7.2   Experimental

Use of 2-Amino Perimidine

This initial study required (1) Envelope B (AZ-101) simulant, (2) 2-Amino Perimidine, and 5 M sodium hydroxide solution. Envelope B simulant was formulated at the SRTC.[13] Its composition is given in Appendix 3. It contains 4.74 M total sodium and was run without dilution in this experiment. It also

contains 0.014 M chromate, which can potentially interfere with sulfate removal methods. In Envelopes A and C, molybdate (0.0004 – 0.0009 M) is also a potential source of interference.

25 grams of 2-AP (hydrobromide form, CAS #40835-96-9) was obtained from Fluka. Its molecular weight is 291.16 g/mole, though removal of the hydrobromide provides a freebase material with molecular weight 183.23 g/mole.

The basic steps for the scoping tests were:

1. Contact 3 grams of 2-AP (hydrobromide form) with 5 M NaOH at room temperature (total slurry volume 20 ml) and mix each for 20 minutes. This is to remove the hydrobromide.

2. Filter the solid from the NaOH and use fresh NaOH for a total of 3 contacts.

3. Contact the freebased solid with 100 ml of simulant at room temperature. Mix for 2 hours at room temperature.

4. The solids were filtered and the treated simulant (filtrate) was placed in a sample bottle.

5. Here a mistake was made - the solid was contacted with 100 ml of a second portion of simulant instead of NaOH elution liquid. This mixture was filtered immediately. The filtrate was returned to the simulant stock bottle because there was not enough simulant for the second treatment without it. The simulant stock bottle was sampled after mixing.

6. The solid was regenerated with three 20 ml portions of 5 M NaOH as before.

7. 100 ml of simulant from the stock bottle was contacted with the solid for 1 hour.

8. The solids were submitted for nitric acid dissolution and anion plus metal analysis after filtration from the last treatment.

Cobalt Complexes

Since Werner complexes were not available only one simple test was done. Five grams of hexammine cobalt (III) trichloride solid (Mol. Wt. 267.48, 0.0187 mole) was added to 25 ml of Envelope B simulant that had been adjusted to 4 M sodium. This corresponded to 0.75 M cobalt. This excess was assumed to perhaps show sulfate removal through transformations to other complexes. The solid-liquid mixture was stirred for several hours. The mixture was filtered. Filtrate composition was compared with initial feed.
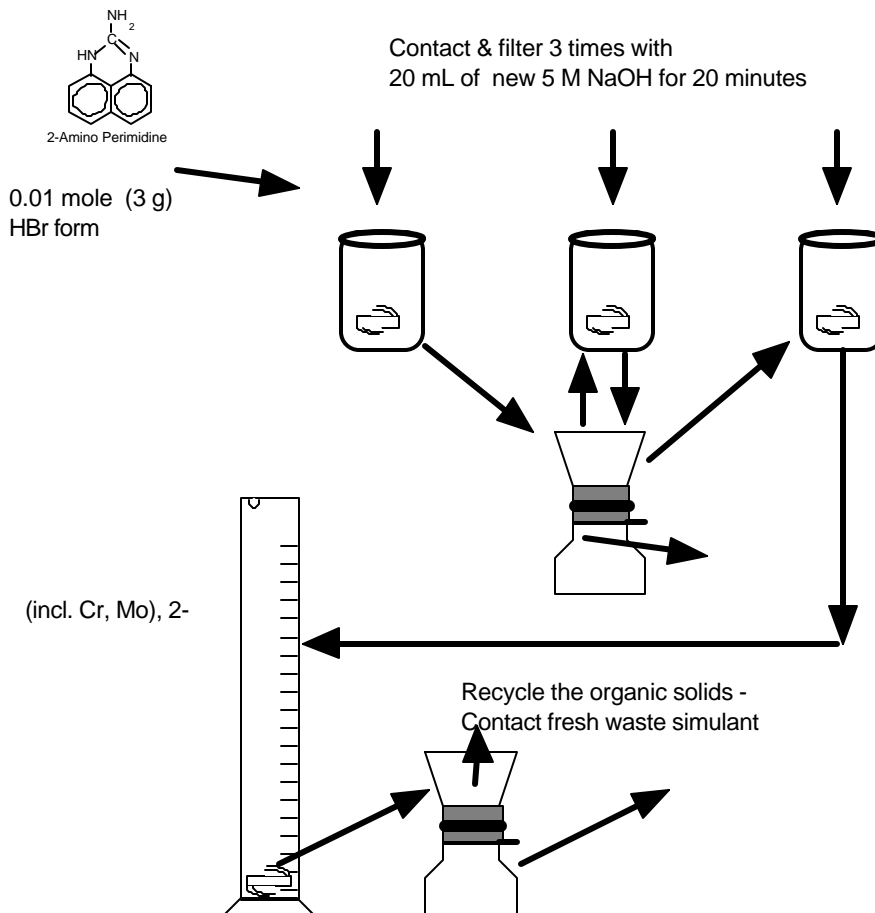
Figure 7.1. 2-Amino Perimidine Washing and Sample Contacting

Low-Temperature Crystallization

Crystallization experiments were performed in three groups, assessing the effects of different simulants, additives and dilution on sulfate removal. Additives were selected to vary ionic strength of the solution, alter water activity, and induce formation of different minerals or salts from the simulants. Dilutions were performed using nitric acid and de-ionized water to assess the effects of varying sodium ion and caustic concentrations on sulfate removal.

A simplified method was used to perform chilled crystallization of simulants.

1. Simulants were made generally by taking the standard recipe for simulants of Tanks AN-105 (Envelope A), AZ-101 (Envelope B), and AN107 (Envelope C) and preparing these to a range of post-Cs and Tc ion exchange conditions with respect to desired sodium level and caustic level.

    A. Undiluted and untreated simulants had the following composition:

        -   Envelope A: 5.0 M Na, 1.6 M free OH-

        -   Envelope B: 4.74 M Na, 0.52 M free OH- (additive tests)

        -   Envelope B: 4.9 M Na, 0.66 M free OH- (dilution tests)

        -   Envelope C: 5.9 M Na, 0.96 M free OH-

    B. Diluted Envelope B simulants were prepared from 4.9 M Na, 0.66 M free OH- Envelope B simulant

        -   4.1 M Na, 0.2 M free OH- (1.2 ml 60 wt.% HNO3 and 8.1 ml de-ionized water added per 45 ml 4.9 M Na simulant)

        -   3.0 M Na, 0.2 M free OH- (0.8 ml 60 wt.% HNO3 and 21.8 ml de-ionized water added per 45 ml 4.9 M Na simulant)

2. 30 gram aliquots of the prepared liquids were put in labeled 40-ml glass vial.

3. In the additive test with Envelope B simulant (4.74 M Na), the following were prepared:

-        Untreated 30 g simulant + 1.0 g NaOH

-        Untreated 30 g simulant + 1.4 g KOH

-        Untreated 30 g simulant + 3 g isopropyl alcohol

-        Untreated 30 g simulant + 0.1889 g NaF + 0.2630 g NaCl

-        Untreated 30 g simulant + 2.53 g of 2:5 polymer solution:DI H2O mixture

4. Vials were placed in a beaker with some of the glycerin/water mixture used in the cooling bath, which was used as a secondary heat transfer agent. A thermometer used for recording vial temperature was placed in the beaker adjacent to the vials.

5. The beaker was either placed in a laboratory chiller containing 40 wt.% glycerin in water (lowest available temperature –22° C), or was placed in a Styrofoam bucket of dry ice/60 wt.% glycerin in water mixture in cases where samples did not form sufficient crystals within the specified 3-5 hours chilling time in the lab chiller.

6. The vials were chilled until half to three quarters of the liquid was frozen. If the vial was frozen to too great an extent, the vial was removed from the bath and was allowed to warm at room temperature slowly until sufficient liquid was generated.

7. When a vial had frozen to a sufficient extent, a long, thin hypodermic needle and plastic syringe was used to draw liquid from the cold sample. The goal was to remove as much liquid as possible without melting any of the crystals. The method was effective at removing liquid at the low temperature but was not effective at extracting every last drop of liquid from the slush.

8. The syringe was immediately discharged into a clean glass vial. Vials of drained slush and liquid product were allowed to warm to room temperature.

8. Vials were submitted to Analytical Development Section (ADS) for ICP-ES, IC-Anions, TIC/TOC, and carbonate analysis.

The test specification describes the data reporting and data quality requirements for the task.[14]

7.3   Results and Discussion

2-Amino Perimidine Experimental Results

Physical Results

2-AP is a fine gray powder as received. It mixed into the caustic and the simulant with moderate difficulty. It tended to form a floating froth layer though it did not separate well in either solution. On this small scale it does not look like flotation would be practical for solid-liquid separation, though larger scales and time may make a difference. The decision was made to use a filter as soon as the poorly-separating nature of the solids was seen.

The air oxidation of wet 2-AP in these solutions is notable. While the initial slurry showed the gray color, slurry films at the top of vessels would turn jet black, notable over several minutes. The 3-gram charge of 2-AP turned black over the 1-day use. There were no attempts to blanket the material from oxygen or to shield it from ambient fluorescent light in the room.

The material was easy to filter. The same 0.45 micron nylon filter was used for each treatment (total of two filters), including three caustic recharges and one waste treatment.

The change in appearance of the 2-AP between NaOH and simulant contacts was striking. Figure 7.2 shows the solid in a filter cup. Filtrate from the NaOH contacts were always dark in color and

contained visible black solids despite the filtration. Filtrates from the treatments were only slightly darkened and there were little if any black solids in them. Solids in the filtrate are believed to be from 2-AP that dissolved in the liquid, got through the filter, then air-oxidized. One interpretation of this is that 2-AP is less soluble in the (sulfate-containing) simulant than in the NaOH regenerants.

Figure 7.2. 2-Amino Pyramidine after Contact with Caustic and Air

Sulfate Removal Results

Removal factors (initial/final ratios of concentrations) of sulfate, chromate, and molybdate in the waste are shown in Table 7.1. The initial three NaOH contactings were intended to remove bromide. Table 7.1 shows the progressive removal. Most of the bromide was removed from the first contact with 5M NaOH. The removal of bromide from the 2-AP as received was essentially complete; none was above detection limits of 100 mg/l after the initial rinsing with the three NaOH washes. Total Organic Carbon (TOC) remained essentially constant for all liquids contacted by the 2-AP.

Table 7.1. Bromide Removal and Total Organic Carbon in Filtrates

	Bromide Replicate-1	Bromide Replicate-2	Average Br, mg/l	TOC Replicate-1	TOC Replicate-2	Average TOC, mg/l
NaOH#1	32393	32329	32361	607	440	524
NaOH#2	6018	5998	6008	249	263	256
NaOH#3	1480	1482	1481	492	325	409
Treated #1	<100	<100	<100	470	525	498

Degree of Removal factors or DF's are defined as (concentration in feed)/(concentration in product), normalized to sodium level to remove dilution effects. Table 7.2 shows that the 2-AP really did not remove significant amounts of the elements that were measured, including sulfur (sulfate). The Second treatment in the table was of the simulant being contacted with recycled 2-AP from the first test. The first test would be expected to show the most removal of sulfate since the 2-AP was freshest there, but the reagent was largely ineffective in doing the job.

Table 7.2. Degree of Removal of Elements from Envelope B Simulant

First Treatment	
Al	0.91
Cr	0.93
Mo	0.93
P	1.09
S	1.03

Second Treatment	
Al	1.08
Cr	1.09
Mo	1.08
P	1.11
S	1.02

Experimental Results with Cobalt Hexammine Ion

All the ICP-ES data for this test is shown below. The use of the hexammine cobalt trichloride dry reagent did show removal of some chromium and silicon, but was not very effective in removing sulfate. The Degree of Removal factor or DF is as defined for the 2-AP work; it uses sodium level to correct for dilution.

While this reagent failed to remove sulfate significantly it is interesting that the cobalt was 0.058 molar in the caustic filtrate. Cobalt hydroxide and carbonate is insoluble in water, so this cobalt is most likely present as complex(es), perhaps having ammine and nitrite ligands. The liquid was rose red. The retained solids were light in color.

Table 7.3. Results from Cobalt Hexammine Ion Treatment on Envelope B Simulant

	Initial	Treated #1	Treated #2	Treated Average	Removal Factor
ADS #>	134568	134569	135469	mg/l	mg/l
Al	7645	7480	7285	7383	1.02
B	<1.0	<1.0	<1.0		
Ba	<0.5	<0.5	<0.5		
Ca	3.2	2.2	<2.0		
Cd	<0.2	<0.2	<0.2		
Co	2.8	3365	3420	3393	0.00
Cr	695	376	366	371	1.84
Cu	<0.5	<0.5	<0.5		
Fe	0.8	1.2	<0.6		
Mn	<0.5	<0.5	<0.5		
Mo	118	111	116	114	1.02
Na	94050	94050	90450	92250	1.00
Ni	<0.6	<0.6	<0.6		
P	478	474	462	468	1.00
Pb	<0.5	<0.5	<0.5		
Si	17	11	11	11	1.49
Sr	<0.5	<0.5	<0.5		
Ti	<0.5	<0.5	<0.5		
Zn	3.4	<0.5	<0.5		
S	2915	2530	2440	2485	1.15

Low Temperature Crystallization Experimental Results

Undiluted/Untreated A, B, and C Simulant Studies

Undiluted/untreated Envelope A (AN-105), Envelope B (AZ-101), and Envelope C (AN-107) simulants were crystallized and liquid phases were removed to examine the change in observed sulfate removal in different simulants, and indirectly examine the effects of different sulfate concentrations. The ICP-ES (Induced-Coupled Plasma-Emission Spectroscopy) analytical results of the decanted liquid and melted crystal phases yielded the following sulfate removals:

Table 7.4. Decontamination Factors, sulfate-to-sodium ratios, and sulfate fractionation at crystallization conditions based on ICP-ES data.

		Na (M)	Free OH⁻ (M)	SO₄ (M)	Final SO₄:Na ratio (x10⁻³)	DF	Decant/Feed (mass)	% Feed S to LAW	Cryst. Temp. (°C)
Env. A	AN-105	5.0	1.60	0.004	0.74	1.05	0.30	34	-34
Env. B	AZ-101	4.7	0.52	0.18	11.9	2.66	0.52	10	-9
Env. B	AZ-101	4.9	0.66	0.18	18.4	2.62	0.32	7.4	-20
Env. C	AN-107	6.0	1.01	0.02	4.1	0.99	0.15	17	-27

Env. A (Uncrystallized)	0.78
Env. B (Uncrystallized, 4.7 M Na)	31.8
Env. B (Uncrystallized, 4.9 M Na)	48.2
Env. C (Uncrystallized)	4.1

where DF (Decontamination Factor) is defined as the feed SO₄:Na ratio divided by the decanted liquid SO₄:Na ratio. The above results indicate that sulfate removal increases with increasing sulfate content in the solution to be treated. In the case of Envelope B, comparison of the decant/feed mass ratio and fraction of S exiting to the LAW shows that sulfur removal was not just solely due to splitting the feed stream into two fractions. With respect to meeting the maximum allowable SO₄:Na ratios, Envelope B results fell just short of the required 9.68×10^{-3} SO₄:Na ratio. Envelopes A and C did not show appreciable sulfate separation between the solid and liquid phases, and were actually already below required limits due to their formulation for work in evaporation studies. A DF was not considered appreciable unless it was below 0.8 or above 1.2, where a 20% change from unity was required due to the propagation of error in the "accuracy to within 10%" guaranteed by ADS. Sulfur mass balance closures on the above results were all above 95%.

As a confirmation of the ICP-ES results and to show the effects of crystallization on other anions, the resulting liquid and melted solid phases were analyzed by ion chromatography (IC-Anions), for

carbonate, and for organic/inorganic carbon. The IC-Anions results for sulfate were similar to the ICP-ES results, and did not qualitatively change the observed results.

Table 7.5. Decontamination Factors, sulfate-to-sodium ratios, and sulfate fractionation at crystallization conditions based on IC-Anions data.

		Na (M)	Final SO_4:Na ratio (x10^{-3})	DF	Decant/Feed (mass)	% Feed S to LAW
Env. A	AN-105	5.0	0.51	1.16	0.30	41
Env. B	AZ-101	4.7	13.7	2.86	0.52	3.9
Env. B	AZ-101	4.9	17.8	2.39	0.32	5.3
Env. C	AN-107	6.0	3.5	1.08	0.15	11

Mass balances for sulfur on the above results were all above 86%. DF values were calculated for the other anions below. Carbonate and phosphate in Envelope A did show a slight tendency to move to the solid phase, although TIC did not support the carbonate data. Envelope C did show a tendency for carbonate to go to the solid phase, where TIC again was neutral. It is believed that the TIC data is being skewed low by somewhat low results obtained for the uncrystallized simulants. In Envelope B where larger sulfate separations were achieved, carbonate and TIC tend to crystallize with the sulfate while phosphate, nitrate, and perhaps nitrite tend to stay in the liquid phase. Envelope B formate and oxalate levels were below detection limits (100 µg/ml), and TIC/TOC concentrations were either not measured or were below detection limits (200 ppm).

Table 7.6. Calculated Decontamination Factors (DF) for other analyzed anions in undiluted/untreated simulants based on IC-Anions data.

	Average Calculated DF for									
	PO_4^{3-}	TIC	CO_3^{2-}	Cl^-	F	NO_3^-	NO_2^-	$HCOO^-$	$C_2O_4^{2-}$	TOC
Env. A	1.24	0.88	1.21	1.12	1.07	1.03	1.14	0.95	1.19	1.02
Env. B (4.7 M)	0.64	----	1.96	1.72	0.99	0.80	0.73	----	----	----
Env. B (4.9 M)	0.71	1.41	8.46	0.46	0.74	0.67	0.82	----	----	----
Env. C	1.19	1.06	1.43	0.96	1.00	0.95	0.97	0.98	0.95	0.92

Phosphate DF's calculated from ICP-ES results ranged from 0.79 to 0.81, and appear to support the IC-Anion results. Of the major metals of concern in the simulants (Al, Cr), Al only showed significant movement in the Envelope B samples, where the DF range was 0.76-0.79.

Additive Studies

An Envelope B (AZ-101) simulant was tested with the following materials and motivations:
- No additive (Control sample)

- NaOH (raise free OH- by 1 M)

- KOH (raise free OH- by 1 M, check formation of Hanksite $Na_{22}(SO_4)_9(CO_3)_2KCl$)

- 10 wt.% isopropyl alcohol (change water activity, attempt formation of sulfate phase)

- equimolar NaF/NaCl (attempt formation of Sulfohalite $Na_6ClF(SO_4)_2$)

- cationic polymer (attempt polymeric sulfate salt formation)

The samples were crystallized and decanted as described previously. The resulting DF values obtained from ICP-ES data show that additives did not improve removal of sulfate from the liquid phase for all cases.

Table 7.7. Decontamination Factors, sulfate-to-sodium ratios, and sulfate fractionation at crystallization conditions based on ICP-ES data.

Envelope B +	Na (M)	Free OH⁻ (M)	SO₄ (M)	Final SO₄:Na ratio (x10⁻³)	DF	Decant/ Feed (mass)	% Feed S to LAW	Cryst. Temp. (°C)
Blank	4.7	0.52	0.18	11.9	2.66	0.52	10.1	-9
NaOH	5.7	1.48	0.18	27.5	1.16	0.52	52.9	-10
KOH	4.5	1.31	0.18	37.2	0.85	0.38	63.2	-10
Isopropyl alc.	4.2	0.46	0.16	19.7	1.62	0.52	39.7	-9
NaF/Cl	4.0	0.42	0.15	29.6	1.08	0.81	35.3	-12
Polymer	4.3	0.47	0.17	23.2	1.37	0.65	-----	-12
Uncrystallized	4.7	0.52	0.18	31.8				

Calculated sulfate DF values using IC-Anion data were within 0.2-0.3 of those calculated from ICP-ES data, and mirrored the above finding. IC-Anion data and carbonate data show that in the untreated simulant, carbonate and chloride follow the sulfate into the solid phase, and nitrite and phosphate stay in the liquid phase during crystallization. Upon adding additional free hydroxide, carbonate and nitrite separation fell, phosphate separation disappeared (KOH) or reversed (NaOH), and chloride tendency remained the same. Addition of alcohol improved carbonate and phosphate separation into the solid phase. Polymer addition pushed chloride into the liquid phase, and improved carbonate separation into the solid phase slightly. Addition of Cl/F appeared to eliminate phosphate and chloride separation, while slightly improving fluoride separation. TIC/TOC analyses were not performed, and formate and oxalate anion concentrations were below minimum detection limits (100 µg/ml).

Table 7.8. Calculated Decontamination Factors (DF) for other analyzed anions in the additives study based on IC-Anions data.

Additive	Calculated DF for					
	PO_4^{3-}	CO_3^{2-}	Cl^-	F^-	NO_3^-	NO_2^-
None (Blank)	0.64	1.96	1.72	0.99	0.80	0.73
NaOH	1.22	1.48	2.57	1.28	1.19	1.10
KOH	0.71	1.31	1.70	0.99	0.94	0.86
Isopropyl alc.	5.18	7.70	1.72	1.32	0.81	0.75
NaF/Cl	0.90	0.75	1.09	1.44	1.21	1.11
Polymer	0.82	2.14	0.05	1.19	0.94	0.87

Envelope B Simulant Dilution Studies

Envelope B (AZ-101) simulant (4.9 M Na, 0.66 M free OH-) was diluted to the following Na and free OH- concentrations to examine the effect of these ions on sulfate separation:

- 4.1 M Na, 0.2 M free OH-

- 3.0 M Na, 0.2 M free OH-

The resulting liquid and solid phases were then analyzed by ICP-ES to determine sulfate removal:

Table 7.9.   Decontamination Factors, sulfate-to-sodium ratios, and sulfate fractionation for different Envelope B dilutions at crystallization conditions based on ICP-ES data.

Na (M)	Free OH (M)	SO_4 (M)	Final SO_4:Na ratio ($\times 10^{-3}$)	DF	Decant/Feed (mass)	% Feed S to LAW	Cryst. Temp. (°C)
4.9	0.66	0.18	18.4	2.62	0.32	7.4	-20
4.1	0.2	0.15	22.2	2.17	0.40	25.3	-22
3.0	0.2	0.11	31.6	1.57	0.28	45.6	-22
4.9	0.66	0.18	48.2	Uncrystallized			
4.7	0.52	0.18	11.9	2.66	0.52	10.1	-9
4.7	0.52	0.18	31.8	Uncrystallized			

Sulfur mass balances were closed to within 10% in Table 7.9. Similar to the undiluted simulants, separation of sulfate into the solid phase determined by calculated DF values shows that degree of removal decreases with decreasing sulfate content in the original solution. Similarly, DF drops with decreasing sodium content, and possibly to a lesser degree with free hydroxide. Aluminum tended slightly to the liquid phase during crystallization (DF=0.79), but this phenomenon disappeared upon dilution.

Confirming the ICP-ES data with IC-Anion data, sulfate DF again falls with decreasing sulfate, sodium, and free hydroxide content.

Table 7.10.   Decontamination Factors, sulfate-to-sodium ratios, and sulfate fractionation for different Envelope B dilutions at crystallization conditions based on IC-Anions data.

Na (M)	Free OH (M)	SO_4 (M)	Final SO_4:Na ratio ($\times 10^{-3}$)	DF	Decant/Feed (mass)	% Feed S to LAW	Mass Balance Closure (%)
4.9	0.66	0.18	17.8	2.39	0.32	5.3	6.4
4.1	0.2	0.15	16.4	2.16	0.40	16	-0.6
3.0	0.2	0.11	30.8	0.87	0.28	0.8	21
4.9	0.66	0.18	48.2	**Uncrystallized**			
4.7	0.52	0.18	13.7	2.86	0.52	3.9	10
4.7	0.52	0.18	31.8	**Uncrystallized**			

Dilution factors of 1.19 and 1.63 for the 4.1 M Na and 3.0 M Na solutions, respectively, account for the disparity between final sulfate:sodium ratios and calculated DF. Also the DF for the 3.0 M Na experiment is suspected to be low due to high sulfate numbers obtained in one decant sample.

Using IC-Anion, carbonate, and TIC/TOC data to look at other anions, carbonate tends to follow the sulfate where DF values drop with increasing dilution. TIC follows this trend, but over a lower range. Nitrate, nitrite, fluoride, and chloride all generally tend to the liquid phase during crystallization at all dilutions. Envelope B formate and oxalate levels were below detection limits (100 µg/ml), and TOC concentrations were either not measured or were below detection limits (200 ppm).

Table 7.11. Calculated Decontamination Factors (DF) for other analyzed anions in the Envelope C simulant dilution study based on IC-Anions data.

Na (M)	Average Calculated DF for Anions									
	PO_4^{3-}	TIC	CO_3^{2-}	Cl^-	F^-	NO_3^-	NO_2^-	$HCOO^-$	$C_2O_4^{2-}$	TOC
4.9	0.71	1.41	8.46	0.46	0.74	0.67	0.82	----	----	----
4.1	0.79	1.34	4.32	0.85	0.66	0.77	0.71	----	----	----
3.0	0.51	0.61	1.04	0.39	0.36	0.53	0.54	----	----	----
4.7	0.64	----	1.96	1.72	0.99	0.80	0.73	----	----	----

7.4   Conclusions

The use of 2-amino-perimidine, a cobalt (III) ammine complex, and low temperature crystallization were attempted to remove sulfate from BNFL simulants in preparation for Cs and Tc ion exchange. 2-amino-perimidine and hexammine cobalt (III) trichloride failed to remove significant sulfate. In the case of the 2-AP, literature provides a possible reason for failure: This chemical needs protons to bind with sulfate. Failure implies that other methods based on aromatic amines will not work either. 2-amino perimidine is only one of a class of such chemicals known to extract sulfate from (lower pH) solutions. Low temperature crystallization did lower sulfate levels in treated Envelope B simulants where sulfate levels were high, but not to sufficient levels necessary to meet LAW melter specifications. In Envelope A and C simulants where sulfate levels are lower, low temperature crystallization showed no efficacy.

7.4   References

1.   Stephen, W. I., "A New Reagent for the Detection and Determination of Small Amounts of the Sulphate Ion", Analytica Chim. Acta, vol. 50, pp. 413-422, (1970).

2.   McClure, G. L., "An Improved Synthesis For 2-Amino Perimidine for Use as a Sulfate ,Analytica Chim. Acta, vol. 64, pp. 289-291, (1973).

3.   Williams, W. J., "Handbook of Anion Determination", Butterworths, pp. 535-565, (1977).

4.   Jones, A. S., and Letham, D. S., "A Spectroscopic Method for the Determination of Sub-Micro Quantities of Sulphur with 4-Amino-4'-Chlorodiphenyl", Analyst, vol. 81, pp. 15-18, January, 1956.

5.   Belcher, R., Stephen, W. I., and Nutten, A. J., "Reagents for the Precipitation of Sulfate", Journal of the Chemical Society, pp. 1334-1337, (1953).

6.   Mahr, C., and Krauss, K., Z., "A New Method For Determining Sulfate", Analytical Chemistry, vol. 128, p. 477 (1948).

7.   Belcher, R., and Gibbons, D., "A New Reagent for the Precipitation of Sulfate", Journal of the Chemical Society, pp. 4216-4218, (1952).

8.   Mori, M., Weil, J., and Ishiguro, M., "The Formation of and Interrelation Between Some u-Peroxo Binuclear Cobalt Complexes", Journal of the American Chemical Society, vol. 90 , pp. 615-621, January 1968.

9.   Rousseau, R. W., "Crystallization", Encyclopedia of Chemical Technology, 4th ed., Vol. 5, J. Wiley and Sons, New York, pp. 683-729, (1993).

10.   Cannella, W. J., "Xylenes and Ethylbenzene", Encyclopedia of Chemical Technology, 4th ed., Supplement, J. Wiley and Sons, New York, pp. 844, (1998).

11.   Herting, D. L., "Clean Salt Process Final Report", Report No. WHC-EP-0915, Westinghouse Hanford Company, Richland, WA, September (1996).

12.   Dawson, H. M., "The Ternary System – Sodium Sulphate, Ammonium Sulphate, and Water. The Utilisation of Nitre Cake for the Production of Ammonium Sulphate", J. Am. Chem. Soc., **113**, 675-88, *1918*.

13. C. A. Nash, "Task Technical and Quality Assurance Plan for Simulant Development in Supportof BNFL Part B", BNF-003-98-011, rev. 0, October 5, 1998.

14. M. E. Johnson, River Protection Project Test Specification for Evaluating Sulfate Separation from LAW Solutions, TSP-W375-99-00012, Rev. 0, September 10, 1999.

8.0 Feed Stream Evaporation and Waste Glass Formulation for a Sulfate Pretreated Envelope C AN-102 Sample

8.1 Introduction

As part of the present Part B-1 SRTC demonstration, the Immobilization Technology Section (ITS) of SRTC was tasked to demonstrated, using a crucible-scale furnace, the vitrification portion of the process to producing an ILAW glass waste form from Hanford Tank 241-AN-102. This small active vitrification task evaporates and vitrifies samples from radioactive waste treatment demonstrations being performed by SRTC as part of a Work for Others (WFO) agreement.[1-4] The objectives of the evaporation testing are to produce a concentrated feed for glass formulation and to determine if significant solids formed during evaporation. The objectives of the crucible scale vitrification tests are to demonstrate vitrification of a durable Low Activity Waste glass that meets target specifications of the RPP-WTP.

Earlier work in this Part B-1 program investigated sulfate removal from a portion of the AN-102 decontaminated supernate. The resulting sulfate-pretreated AN-102 supernate product was concentrated by evaporation and the resulting concentrate and condensate were analyzed. Results of the analytical characterization were transmitted to Vitreous State Laboratory (VSL) for glass formulation. However, it was decided by RPP-WTP personnel that sulfate removal by pretreatment was not to be pursued. Thus vitrification of the resulting glass former recipe developed by VSL for the sulfate-treated Env. C AN-102 decontaminated supernate was not completed. This section reports on the evaporation, characterization and glass formulation of the sulfate-treated Env. C, AN-102 sample.

8.2 Experimental

The goal of the Feed Stream Evaporation and Waste Glass Formulation phase was to concentrate the decontaminated sulfate pretreated Envelope C liquid by a factor of ~4.5X and to analyze the resulting concentrate and condensate. The expected concentration endpoint of 80% of bulk saturation @ 25°C was determined based upon the simulant evaporation studies and OLI modeling.[5] The AN-102 LAW liquid was decontaminated of Sr and transuranics by manganese-based Sr/TRU precipitation and filtration. The AN-102 LAW liquid was decontaminated of Cs and Tc by ion exchange pretreatment. Final sulfate decontamination was also performed with a barium-based precipitation method as described elsewhere in this document. The final resulting pretreated AN-102 LAW supernate feed was evaporated to the predicted concentration endpoint and the concentrate was analyzed. A glass formulation was prepared and the concentrate was to be mixed with glass-forming chemicals to complete the feed stream preparation phase.

Decontaminated Liquid Feed Evaporation

A schematic of the evaporator used to concentrate the sulfate pretreated AN-102 sample is shown in Figure 8.1. This 'pot' evaporation unit was operated in a single batch mode, *i.e.*, no continuous feed. This apparatus is designed to incorporate some of the same design elements used in a concurrent bench scale LAW simulant evaporation program ongoing at SRTC.[5] Evaporations were performed at reduced pressure (40 – 80 Torr) provided by a diaphragm pump at nominally 50 C. Preliminary leak testing in the setup showed approximately 1.5 inches of Hg pressure loss over a 24-hour period. This air inleakage equals 1.6E-03 atm cm^3/s, or about 0.21% of system volume. Both the primary and secondary chillers in the evaporation unit were cooled by separate water chiller units.

Liquid evaporation equipment included a central-placed heater rod (Watlow FIREROD, 3/8" diameter x 18" length, equipped with Type K thermocouple, 500 Watt total capacity over ~ 4" length, or 30 cm^2 surface area), vacuum pump (Vacuubrand chemistry diaphragm pump, Model MZ 2C), voltage and current monitoring device (Cole-Parmer DC/AC Model 26840-20 Multimeter), pressure gauge (Ashcroft ASME Test Grade 2A, 0.5% accuracy) and temperature measuring devices (Cole-Parmer Digi-Sense platinum RTD thermometry systems). The pressure gauge, heater rod thermocouple, voltage and current monitoring device, and RTD thermometry systems were all calibrated before use by the SRTC standards lab to NIST-traceable standards. Results of these calibrations are routinely maintained by a calibration coordinator in the ITS of SRTC.

Power to the heated rod was controlled via a variable power supply. Both voltage and current input to the heating rod was monitored and controlled. Evaporation details such as endpoint targets and operating procedures were determined from other ITS studies involving evaporation experiments on simulant streams.[5] Control parameters that were monitored during evaporation activities were: pot temperature, pressure, voltage, current and condenser exit temperatures.

Condensate was collected below the primary condenser and the concentrate was collected in the large heated pot. After the batch evaporation experiment, the system was allowed to cool to ambient temperature. Both concentrate and condensate samples were then obtained and analyzed according to Table 8.1 shown below.

Table 8.1. Required Analytical Support

Technique	Characterize Concentrate and Condensate	Technique	Characterize Concentrate and Condensate
ICP-ES	X	Sr-90	X
AA(Na/K)	X	Tc-99	X
ICP-MS	**X**	TIC/TOC	X
IC	X	Weight% solids	X
Gamma-PHA	X	$AlO_2 + CO_3$ + Free OH	X
Beta-Scint.	X		
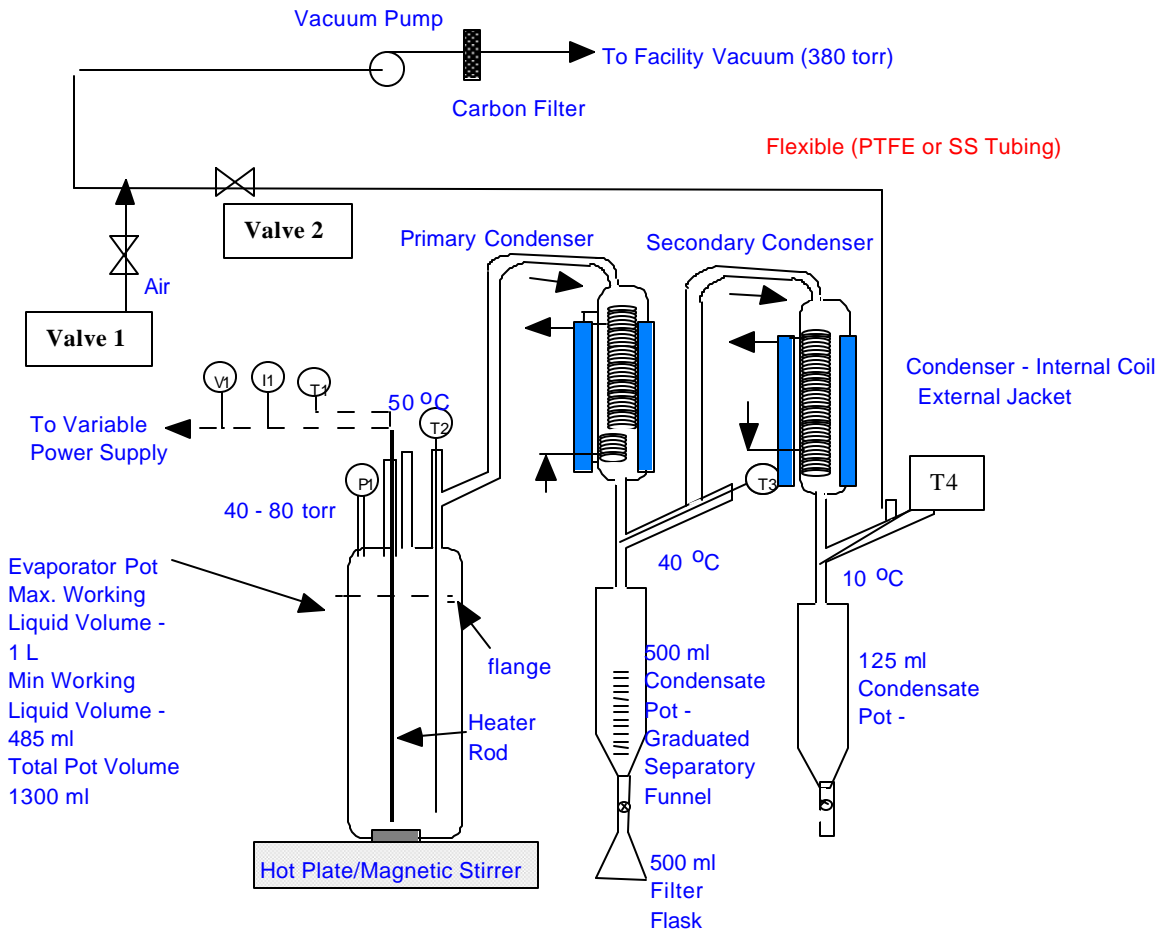
Figure 8.1.   Small LAW Pot Evaporator

Notes:

V1/I1 = Variable voltage and current input to heating rod

P1 = Vacuum pressure gauge

T1 = Type K thermocouple temperature measurement

T2 = RTD temperature readout in Concentrate Pot

T3, T4 = RTD temperature measuring devices in primary and secondary condenser exits, respectively

Valve 1 = air inleakage port controller

Valve 2 = system vacuum on/off

Waste Glass Formulation

This step prepares the appropriate amount of melter feed for the crucible vitrifications.
Concentrated AN-102 supernate was analyzed in duplicate with an AN-107 matrix matched standard according to the analyses shown in Table 8.1. Results from these analyses were transmitted to VSL, who then communicated to SRTC the appropriate amounts of the waste streams, composition of the glass-forming chemicals, and appropriate amounts of the glass-forming chemicals. RPP-WTP personnel reviewed the recommendations and decided to suspend any further task development for glass vitrification with the sulfate pretreated AN-102 concentrated supernate.

8.3   Results and Discussion

Decontaminated Liquid Feed Evaporation

The sulfate pretreated Env. C AN-102 sample was received with the analytical characterization shown in Table 8.2 below. The decontaminated sample was received in a 2-Liter bottle with the label:

[Small C Sulfate Removal, BNFC323, SO4 PPT Filtrate, Weight 851.73g,

Date 1-18-00, Custodian: N. Hassan]

A simple simulant for scope testing of the evaporator was formulated based on the major analytes of the AN-102 sample, i.e., barium, aluminum, sodium, nitrate, nitrite and hydroxide. The simulant supernate composition is also shown in Table 8.2. The salts were dissolved in 0.25 L of ASTM water. Resulting concentrations of the metals Na, Ba, Al and anions nitrate and nitrite are shown in Table 8.2.

The analytical data set for the decontaminated AN-102 sample in Table 8.2 was transmitted to Alex Choi of ITS for modeling to predict the endpoint and operating parameters for the evaporation of AN-102 evaporator feed. Table 8.3 below summarizes the calculation results to determine water removal based on OLI calculations. The model predicted that to reach 80% of saturation, ~ 80% of water from the radioactive pretreated AN-102 feed would have to be removed, concentrating it to 32.38 wt% total solids.

Table 8.2. Analytical Characterization of Pretreated AN-102

Characterization data for small C (AN-102) product		Simple Simulant
LIMS #	3-137448	
Density (g/mL)	1.069	
wt.% soluble solids	8.740	
Cs-137 (uCi/mL)	0.014	
Tc-99 (mg/L)	5.81E-01	
total alpha (dpm/ml)	-	
Sr-90 (dpm/mL)	-	
AA analysis (mg/L)		
K	2.10E+02	
AS	4.33E-02	
SE	1.58E-01	
Hg	< 1.10E-01	
Free OH	1.88E-01	
Carbon (mg/L)		
inorganic (TIC)	415.0	
Organic (TOC)	3304.0	
IC (mg/L)		
NO_3^-	4.03E+04	40,300 (NaNO3)
NO_2^-	6.76E+03	6,760 (NaNO2)
PO_4	< 1.00E+02	
SO_4	3.50E+01	
Oxalate	1.20E+02	
formate	1.02E+03	
Cl^-	2.84E+02	
F^-	1.58E+02	
ICP-ES (mg/L)		
Ag	< 0.546	
Al	1.43E+03	1,430 (Al(OH)3)
B	< 3.76E+00	
Ba	6.53E+02	650 (Ba(NO3)2)
Be	< 9.10E-02	
Ca	1.44E+01	
Cd	5.54E+00	
Ce	< 2.87E+01	
Co	< 4.55E-01	
Cr	2.02E+00	
Cu	1.70E+00	
Fe	4.13E-01	
La	< 1.00E+00	
Li	< 1.82E-01	
Mg	1.00E-01	
Mn	< 9.10E-02	
Mo	5.28E+00	
Na (Molar)	1.15E+00	
Na	2.63E+04	26,300 (NaOH,NaNO3,NaNO2)
Ni	3.20E+01	
P	< 1.24E+01	
Pb	1.15E+01	
Sb	< 6.01E+00	
Si	5.88E+01	
Sn	< 1.37E+00	
Sr	6.19E-01	
Ti	< 1.82E-01	
TI	< 1.22E+01	
V	< 2.73E-01	
Zn	2.74E+00	
Zr	< 3.64E-01	

Table 8.3. Active AN-102 Evaporation Calculations to Determine Water Removal Based on OLI Calculations

Active AN-102 (Small C) Evaporation: Calculations to Determine Water Removal Based on OLI Calculations

	Feed	Product	Condensate
Salt	96.23 g	96.23 g	0.00 g
Water	1004.84 g	200.97 g	**-803.87 g**
Total	1101.07 g	297.20 g	-803.87 g
Density	1.069 g	calc.=1.3143g/mL	
Volume	1030.0 ml	calc.=226.1 mL	
% soluble solids	8.74%	32.38%	
% water	91.26%	67.62%	
% water removed		80.00%	

Antifoam Required, mg/kg	832.6
Active Antifoam Concentration, wt	100.0%
Antifoam solution to add, g	**0.92 g**

Boilup rate			60.00 g/hr
Kettle Diameter			3.5 inches
Flux, g/cm2-hr			0.06 g/hr-cm2
Flux, lb/ft2-hr			1.98 lb/hr-ft2

NOTES:
Basis for end point determination: boil to 80% of saturation at 25C
Start with 1030 mL of AN102 feed from post-sulfate removal pretreatment
Measured total dissolved solids in feed = 8.74 wt% (No visible solids present)
Measured density of feed = 1.069 g/mL

<u>Env. C Simulant Evaporation</u>

The AN-102 simulant evaporator feed solution was initially evaporated in the evaporation apparatus as it was configured for previous evaporation testing involving a decontaminated Env. A AN-103 sample.[6] Stainless steel wool, a vigreux column and de-entrainment finger were in place and 0.92 grams of antifoam agent (DowCorning 1520-US) was added to the evaporator feed solution. Table 8.4 summarizes the data collected during the ~ 10-hour experiment. Overall evaporation rates can be calculated in the 22:45 to 02:45 time span as 240 mL/ 4 hours, or 60 grams of water per hour. No visible solids were observed when the concentrate was allowed to cool to ambient temperature. No significant foaming was observed during the evaporation. The nominal heat flux to the solution from the heat rod can be calculated from the observed voltage and current, and the approximate 4 inch length and 3/8" diameter of heated rod. Multiplying the voltage of 40 V and current of 1.56 amps, and dividing by the total heated surface area of ~ 30 cm^2, a calculated heat flux value of 2.1 W/cm^2 is obtained.

The final endpoint temperature of the evaporation pot was observed to be 47.6 °C from the thermocouple reading taken from the heatrod (T1). This temperature was consistently observed to be slightly higher by a few degrees Celcius than the RTD probe temperature (T2) at 46.5 °C. The RTD probe was located near the outer surface of the concentrate pot and the heatrod thermocouple was located in between the heating elements of the actual heatrod.

Table 8.4. Simulant AN-102 Evaporation Data

Time	T3 (°C)	T1 (°C)	T2 (°C)	P1 Press. (inchesHg)	Pot Vol. (mL)	Condensate Vol. (mL)	T4 (°C)	Volts* (V1)	Amps* (I1)
2-9-00									
22:45	15.2	32.4	28.9	27.4	640	0	12.6	40	nm
23:15	13.4	43.2	41.7	27.6		20	12.4	40	nm
23:45	13.5	43.2	41.7	27.6		50	12.4	40	1.56
2-10-00									
00:15	13.3	43.9	42.5	27.6		80	12.4	40	nm
00:45	13.3	43.6	42.5	27.6		120	12.4	40	nm
01:15	13.3	44.2	42.7	27.6		145	12.4	40	nm
01:45	13.1	44.3	42.9	27.6		175	12.4	40	nm
02:15	13.1	44.4	43.3	27.6		210	12.4	40	1.56
02:45	-	43.8	43.3	27.6	320	240	-	0	nm
System shut down					Refill pot with simulant				
05:00	14.4	34.2	32.3	27.4	540	0	12.8	40	1.56
05:30	12.8	45.8	44.5	27.5		10	11.7	40	nm
06:15	12.8	46.4	44.9	27.6		70	11.8	40	nm
07:00	12.7	47.2	45.8	27.6		120	11.7	40	nm
08:00	12.6	47.6	46.5	27.6	360	180	11.7	40	0
System shutdown									

Notes:

* Nominal heat flux of 4 inch heated zone of heat rod equal to ~ 2.1 W/cm^2

V1/I1 = Variable voltage and current input to heating rod

P1 = Vacuum pressure gauge on Concentrate Pot

T1 = Type K thermocouple temperature measurement in Concentrate Pot

T2 = RTD temperature readout in Concentrate Pot

T3, T4 = RTD exit temperature measuring devices for primary and secondary condensers, respectively

nm = not measured

Env. C Decontaminated Active Sample Evaporation

The decontaminated AN-102 active evaporator feed solution was initially evaporated in the evaporation apparatus as it was configured for previous evaporation testing involving a decontaminated Env. A AN-103 sample.[6] Stainless steel wool, a vigreux column and de-entrainment finger were in place and 0.9 grams of antifoam chemical (DowCorning 1520-US) was added to the evaporator feed solution. Table 8.5 summarizes the data collected during the first ~ 11-hour experiment (2/22/00) followed by the second stage ~ 6-hour experiment (2/23/00). Overall evaporation rates can be calculated in the 07:00 to 12:00 time span as 260 mL/ 5 hours, or 52 grams of water per hour. No visible solids were observed when the concentrate was allowed to cool to ambient temperature after the initial 6 hour evaporation stage. No significant foaming was observed during the evaporation. The evaporator pot was recharged with fresh feed and the condensate pot was emptied at the 12:30 mark, and evaporation was continued until 19:00. The evaporator was continued from 13:45 until about 19:00. A total of about 490 mL of water was collected in this first stage evaporation.

The evaporator was cooled overnight and restarted on 2/23/00. The second stage evaporation evaporated about ~300 mL of feed (540 mL down to 220 mL) and produced 300 mL of condensate. A total of about 800 mL of condensate was removed in all stages of evaporation. Appendix 4 shows digital pictures of the various stages of evaporation. The nominal heat flux to the solution from the heat rod can be calculated from the observed voltage and current, and the approximate 4 inch length and 3/8" diameter of heated rod. Multiplying the voltage of 40 V and current of 1.56 amps, and dividing by the total heated surface area of ~ 30 cm^2, a calculated heat flux value of 2.1 W/cm^2 is obtained.

The final endpoint temperature of the evaporation pot was observed to be 51°C from the thermocouple reading taken from the heatrod (T1). This temperature was consistently observed to be slightly higher by a few degrees Celcius than the RTD probe temperature (T2) at 50 °C. The RTD probe was located near the outer surface of the concentrate pot and the heatrod thermocouple was located in between the heating elements of the actual heatrod.

Analysis of Evaporation Products

The concentrated AN-102 and the condensate liquids were sampled within days after the evaporation experiment was completed. Analytical methods detailed in Table 8.1 were performed by the Analytical Development Section (ADS) of SRTC. Both the AN-102 concentrate and condensate liquids were sampled in duplicate. The concentrate and matrix match standard was diluted by 10X performed by ITS personnel. A matrix matched standard was also submitted using the simulant AN107 liquid prepared in the sulfate pretreatment program by M. Hay of SRTC. Table 8.7 shows the as batched composition of this matrix match standard. An ASTM-I water sample derived from a Milli-Q water purification system was submitted as the matrix standard for the condensate sample. Results from analysis of the evaporator concentrate and condensate and standards are collected in Tables 8.6 and 8.8, respectively. Concentrate

samples were diluted by ADS personnel before analysis. A dilution factor of 1 to 91 was used for ICP-ES analysis. A dilution factor of 1 to 1000 was used for ICP-MS analysis. The condensate samples were either analyzed as received or diluted 1 to 10 (ICP-MS).

Two different calculations were performed with the average values of the data shown in Tables 8.6 and 8.8. First, the concentration factors calculated from the evaporation process were obtained by dividing the final concentrate average concentrations by the initial feed concentrations. These data are shown in Table 8.9. The concentration factor averaged from 3.8 to 4.4 vs. a target of 4.6. A second calculation was performed to determine the decontamination factor from the evaporation process. The evaporator feed solution concentration values were divided by the average condensate concentration values to determine how well the resulting condensate was decontaminated. These data are shown in Table 8.10. Calculated decontamination factors are in the range of 2E+03 to 2.0E+05 for the various analytes shown in Table 8.10.

Table 8.5. Active AN-102 Evaporation Data

Time	T3 (°C)	T1 (°C)	T2 (°C)	P1 Press. (inches Hg)	Pot Vol. (mL)	Condensate Vol. (mL)	T4 (°C)	Volts * (V1)	Amps * (I1)
2-22-00									
06:30	19	34	32	27.2	550	0	18.2	40	1.55
07:30	18	49	48	27.2	-	50	19	40	1.56
08:30	19	48	47	27.2	450	100	20	40	nm
09:30	19	48	47	27.2	450	140	20	40	1.56
10:30	19	48	47	27.2	350	190	20	40	nm
11:30	19	49	48	27.2	-	240	20	40	1.56
12:30	19	49	48	27.2	240	300	20	40	nm
System Shutdown					AN-102 Added	Condensate Emptied			
13:45	20	26	23	27.4	720	0	20	40	nm
14:45	20	51	49	27.4	700	20	20	40	1.56
15:45	20	51	49	27.0	680	50	20	40	nm
16:45	19	51	49	27.0	650	100	20	40	nm
17:30	19	51	49	27.2	550	140	20	40	1.56
19:00	19	23	23	27.2	520	190	20	0	0
System Shutdown									
2-23-00						Condensate Emptied			
09:15	18	37	36	27.4	540	0	18	40	1.55
10:15	19	52	50	27.4	510	40	20	40	1.56
11:15	19	51	50	27.4	475	70	20	40	nm
12:15	19	52	50	27.2	425	100	20	40	Nm
14:00	19	48	47	27.2	350	180	20	40	1.54
15:00	19	48	47	27.2	280	240	20	40	1.54
System shutdown									
16:45					220	300			

Notes:

* Nominal heat flux of 4 inch heated zone of heat rod equal to ~ 2.1 W/cm^2

V1/I1 = Variable voltage and current input to heating rod

P1 = Vacuum pressure gauge on Concentrate Pot

T1 = Type K thermocouple temperature measurement in Concentrate Pot

T2 = RTD temperature readout in Concentrate Pot

T3, T4 = RTD exit temperature measuring devices for primary and secondary condensers, respectively
  nm = not measured

Table 8.6. AN-102 Concentrate Analyses

AN-102 Concentrate Data		Final Post Evaporator Concentrate Concentrations				AN-107 No-Lead' Batch Recipe Conc.
ICP-ES RESULTS:	dilfac = 10X #139691	dilfac = 10X #139692	Average	% Rel. St.Dev.	dilfac = 10X Matrix Std #139693	
Al	6047.4	6175.55	6111.475	1.5	319.47	387
B	16.42	17	16.71	2.5	34.27	37
Ba	1668.2	1681.95	1675.075	0.6	< 0.2	0
Cd	22.55	22.9	22.725	1.1	0.44	0
Co	2.79	2.65	2.72	3.6	< 0.5	0
Cr	10.88	10.81	10.845	0.5	< 0.7	0
Cu	5.51	5.56	5.535	0.6	26.93	30
Ca	37.58	37.61	37.595	0.1	541.55	591
Fe	2.82	2.55	2.685	7.1	1477.24	1692
La	1.7	1.1	1.4	30.3	45.96	48
Li	0.2	<0.2	<0.20		< 0.2	0
Mg	0.37	0.36	0.365	1.9	46.05	25
Mn	0.1	<0.1	<0.10		504.05	564
Mo	24.01	24.4	24.205	1.1	40.63	40
Na (Molar)	4.94	5.06	5.00		8.86	9.04
Na	113568.9	116334.07	114951.485	1.7	203635.35	207768
Ni	137.06	139.58	138.32	1.3	453.74	533
P	54.26	52.69	53.475	2.1	434.41	363
Pb	50.7	52.89	51.795	3.0	3.58	0
Si	74.86	75.94	75.4	1.0	< 1.6	0
Sn	8.35	7.93	8.14	3.6	20.55	0
Sr	2.25	2.26	2.255	0.3	7.59	7
Ti	0.29	0.23	0.26	16.3	< 0.2	0
V	0.65	0.5	0.575	18.4	< 0.3	0
Zn	5.51	5.66	5.585	1.9	49.68	51
Zr	0.68	0.52	0.6	18.9	51.67	70

	dilfac = 10X #139694	dilfac = 10X #139695	Average	% Rel. St.Dev.	Matrix Std. dilfac = 10X # 139696	
K(AA), mg/L	990.42	959.82	975.12	2.2	2507.415	1812
Na(AA), mg/L	118887.109	115341.396	117114.2525	2.1	202288.262	20777
AL02, Molar	0.263	0.272	0.2675	2.4	in progress	0.01
CO3, Molar	<0.02	<0.02	<0.02		in progress	1.40
Free OH, Molar	0.704	0.701	0.7025	0.3	in progress	0.83
Total wt% Solids	31.64	33.2	32.42	3.4	in progress	49.49
TIC, mg/L	199.8	204	201.9	1.5	14930	16800
TOC, mg/L	6712.2	6420	6566.1	3.1	in progress	40400

IC Anions, mg/L	dilfac = 10X # 139697	dilfac = 10X #139698	Average	% Rel. St.Dev.	Matrix Std. dilfac = 10X # 139699	
Fluoride	740	690	715	4.9	in progress	131
Formate	4540	4240	4390	4.8	10970	10406
Chloride	1300	1210	1255	5.1	1580	1844
Nitrite	34270	31780	33025	5.3	48700	61014
Nitrate	162190	149310	155750	5.8	210090	231765
Phosphate	<1000	<1000	<1000		<1000	1112
Sulfate	<500	<500	<500		<500	0
Oxalate	<1000	<1000	<1000		<1000	834
Gamma PHA						
Cs-137, uCi/mL	0.06129	0.06197	0.06163	0.8	< 0.0000347	0
Co-60, uCi/mL	0.03007	0.03036	0.030215	0.7	< 0.0000752	0
Tc-99, uCi/mL	0.04954955	0.05	0.049774775	0.6	< 0.000130631	0
Sr-90, uCi/mL	0.00113964	0.001283784	0.001211712	8.4	< 0.000274775	0

ICP MassSpec Mass Number	dilfac = 10X #139691	dilfac = 10X #139692	Average	% Rel. St.Dev.	Matrix Std. dilfac = 10X # 139693	
230	<2.8	<2.8	<2.8		<2.8	0
231	<2.8	<2.8	<2.8		<2.8	0
232	202.3	204.5	203.4	0.8	7.1	0
233	<2.8	<2.8	<2.8		<2.8	0
234	<2.8	<2.8	<2.8		<2.8	0
235	<2.8	<2.8	<2.8		<2.8	0
236	<2.8	<2.8	<2.8		<2.8	0
237	2.9	3.2	3.05	7.0	<2.8	0

Table 8.7.   Matrix Simulant of AN-107

| | 1000 | mL |

Formula	Formula Wt	Actual Mass, grams	Moles	Water, grams	Solids Mass	Na, Moles	Metal	mg/Liter
Al(NO3)3.9H2O	375.13	5.38	1.43E-02	2.3253	3.0547		Al	387
NH4Ch3COO	77.08		0.00E+00		0.0000		NH4+	0
Ba(NO3)2	261.35		0.00E+00		0.0000		Ba	0
H3BO3	61.83	0.21	3.40E-03		0.2100		B	37
Ca(NO3)2.4H2O	236.15	3.48	1.47E-02	1.0619	2.4181		Ca	591
Ce(NO3)3.6H2O	434.23	0.17	3.91E-04	0.0423	0.1277		Ce	55
CsNO3	194.91	0.028	1.44E-04		0.0280		Cs	19
Cu(NO3)2.2.5H2O	232.59	0.11	4.73E-04	0.0213	0.0887		Cu	30
Na2EDTA.2H2O	372.24	7.26	1.95E-02	0.7027	6.5573	3.90E-02	EDTA	5621
Fe(NO3)3.9H2O	404	12.24	3.03E-02	4.9123	7.3277		Fe	1692
HEDTA	278.26	2.16	7.76E-03		2.1600		HEDTA	2137
La(NO3)3.6H2O	433.03	0.15	3.46E-04	0.0374	0.1126		La	48
Pb(NO3)2	331.2		0.00E+00		0.0000		Pb	0
Mg(NO3)2.6H2O	256.41	0.26	1.01E-03	0.1096	0.1504		Mg	25
MnCl2.4H2O	197.9	2.03	1.03E-02	0.7392	1.2908		Mn	564
Nd(NO3)3.6H2O	438.35	0.3	6.84E-04	0.0740	0.2260		Nd	99
Ni(NO3)2.6H2O	290.81	2.64	9.08E-03	0.9813	1.6587		Ni	533
KNO3	101.1	4.6	4.55E-02		4.6000		K	1812
Sr(NO3)2	211.63	0.017	8.03E-05		0.0170		Sr	7.0
Zn(NO3)2.6H2O	297.47	0.23	7.73E-04	0.0836	0.1464		Zn	51
	249.23	0.19	7.62E-04		0.1900		Zr	70
HOCH2COOH, 70 wt%	76.05	26.94	2.48E-01	8.0820	18.8580		Glycolate	18608
	218.14	43.64	2.00E-01		43.6400	2.00E-01	Gluconate	39041
	210.14	9.44	4.49E-02		9.4400		Citrate	8495
	191.14	0.57	2.98E-03		0.5700		NTA	561
	133.1	6.05	4.55E-02		6.0500		IDA	5958
NaCl	58.44	1.84	3.15E-02		1.8400	3.15E-02	Cl	1844
NaF	41.99	0.29	6.91E-03		0.2900	6.91E-03	F	131
Na2CrO4	161.97		0.00E+00		0.0000	0.00E+00	Cr	0
Na2CO3	105.99	148.25	1.40E+00		148.2500	2.80E+00	CO3=	83936
NaOH	40	33.28	8.32E-01		33.2800	8.32E-01	OH-	14150
NaNO2	69	91.51	1.33E+00		91.5100	1.33E+00	NO2-	61014
Na3PO4.12H2O	380.12	4.45	1.17E-02	2.5308	1.9192	3.51E-02	PO4-3	1112
K2MoO4	238.14	0.1	4.20E-04		0.1000		Mo	40
Na2SO4	142.04		0.00E+00		0.0000	0.00E+00	SO4=	0
NaHCOO	68.01	15.72	2.31E-01		15.7200	2.31E-01	HCOO-	10406
NaCH3COO.3H2O	136.08	2.38	1.75E-02	0.9452	1.4348	1.75E-02	CH3COO-	1033
Na2C2O4	134	1.27	9.48E-03		1.2700	1.90E-02	C2O4=	834
NaNO3	84.99	297.6	3.50E+00		297.6000	3.50E+00	NO3-	231765
		724.785		22.6490	702.1360	9.0374		

| | 1418.6 | grams |

| | 1.419 | g/mL |

| | 49.49 | % |

| | 9.04 | Molar |

| | 20777 | mg/Liter |

Table 8.8. AN-102 Condensate Analyses

ICP-ES RESULTS:		#139700		#139701		Average	%Rel Std.Dev.		Matrix Std. ASTM-I Water #139702
Condensate Concentrations									
Al		0.087		0.055		0.071	31.9		0.069
B		0.007	<	0.005		0.006	23.6	<	0.005
Ba		0.003	<	0.002		0.0025	28.3		0.003
Cd	<	0.003	<	0.003	<	0.003	0.0	<	0.003
Co		0.008		0.006		0.007	20.2		0.007
Cr	<	0.007	<	0.007	<	0.007	0.0	<	0.007
Cu	<	0.003	<	0.003	<	0.003	0.0		0.005
Ca		0.031		0.031		0.031	0.0		0.038
Fe		0.006		0.005		0.0055	12.9		0.006
La	<	0.011	<	0.011	<	0.011	0.0	<	0.011
Li		0.003		0.003		0.003	0.0		0.003
Mg	<	0.001	<	0.001	<	0.001	0.0	<	0.001
Mn	<	0.001	<	0.001	<	0.001	0.0	<	0.001
Mo	<	0.006	<	0.006	<	0.006	0.0	<	0.006
Na (Molar)		1.74E-05		1.01E-05		1.37E-05			1.29E-05
Na		0.399		0.233		0.316	37.1		0.297
Ni		0.013	<	0.007		0.01	42.4		0.009
P	<	0.026	<	0.026	<	0.026	0.0	<	0.026
Pb		0.037		0.03		0.0335	14.8		0.041
Si		0.262		0.258		0.26	1.1		0.025
Sn	<	0.015	<	0.015	<	0.015	0.0	<	0.015
Sr	<	0.001	<	0.001	<	0.001	0.0	<	0.001
Ti		0.005		0.003		0.004	35.4		0.004
V		0.008		0.007		0.0075	9.4		0.007
Zn	<	0.003	<	0.003	<	0.003	0.0		0.005
Zr		0.009		0.007		0.008	17.7		0.007

	#139703	#139704	Average	StDev	#139705
K(AA), mg/L	<0.1350	<0.1350	<0.1350		<0.1350
Na(AA), mg/L	0.18	0.18	0.18	0.0	0.18
AL02, Molar	<0.002	<0.002	<0.002		<0.002
CO3, Molar	<0.002	<0.002	<0.002		<0.002
Free OH, Molar	<0.002	<0.002	<0.002		<0.002
TIC, mg/L	2.665	in progress			in progress
TOC, mg/L	11.145	in progress			in progress

IC Anions, mg/L	#139706	#139707	Average	#139708
Fluoride	<0.2	<0.2	<0.2	<0.2
Formate	<1	<1	<1	<1
Chloride	<0.2	<0.2	<0.2	<0.2
Nitrite	<1	<1	<1	<1
Nitrate	<1	<1	<1	<1
Phosphate	<1	<1	<1	<1
Sulfate	<0.5	<0.5	<0.5	<0.5
Oxalate	<1	<1	<1	<1

Gamma PHA							Average		
Cs-137, uCi/mL	<	0.00000508	<	6.65E-06	<	5.87E-06		<	6.18E-06
Co-60, uCi/mL	<	0.00000514	<	1.89E-06	<	3.52E-06		<	5.77E-06
Tc-99, uCi/mL	<	1.53153E-05	<	1.31E-05	<	1.42E-05		<	1.31E-05
Sr-90, uCi/mL	<	2.74775E-05	<	2.75E-05	<	2.75E-05		<	2.75E-05

ICP-Mass Spec. ug/L Mass #	#139700	#139701	Average	#139702
230	<0.28	<0.28	<0.28	<0.28
231	<0.28	<0.28	<0.28	<0.28
232	<0.28	<0.28	<0.28	<0.28
233	<0.28	<0.28	<0.28	<0.28
234	<0.28	<0.28	<0.28	<0.28
235	<0.28	<0.28	<0.28	<0.28
236	<0.28	<0.28	<0.28	<0.28
237	<0.28	<0.28	<0.28	<0.28
238	<0.28	<0.28	<0.28	<0.28
239	<0.28	<0.28	<0.28	<0.28
240	<0.28	<0.28	<0.28	<0.28
241	<0.28	<0.28	<0.28	<0.28
242	<0.28	<0.28	<0.28	<0.28

Table 8.9. Concentration Factors Calculated from Evaporation of AN-102

AN-102 Evaporation: Feed & Concentrate Compositions; Concentration Factor			
	AN-102 Evap. Feed	**Concentrated AN102 Product**	**Concentration Factor**
Wt.% soluble solids	8.740	32.42	3.7
AA analysis (mg/L)			
K	209.5	975.1	4.7
Free OH	0.2	0.7	3.7
Carbon (mg/L)			
Inorganic (TIC)	415.0	201.9	0.5
Organic (TOC)	3304.0	6566.1	2.0
IC (mg/L)			
NO_3^-	40330.0	155750.0	3.9
NO_2^-	6759.0	33025.0	4.9
HCO2-	1023.0	4390.0	4.3
Cl^-	284.0	1255.0	4.4
F^-	158.0	715.0	4.5
ICP-ES (mg/L)			
Al	1432.8	6111.5	4.3
Ba	652.6	1675.1	2.6
Cd	5.5	22.7	4.1
Cr	2.0	10.8	5.4
Cu	1.7	5.5	3.3
Ca	14.4	37.6	2.6
Fe	0.4	2.7	6.5
Mg	0.1	0.4	3.7
Mo	5.3	24.2	4.6
Na (Molar)	1.1	5.0	4.4
Na, mg/L	26326.9	114951.5	4.4
Ni	32.0	138.3	4.3
Pb	11.5	51.8	4.5
Si	58.8	75.4	1.3
Sr	0.6	2.3	3.6
Zn	2.7	5.6	2.0

Average Concentration Factor
Based on ICP-ES Metals   **3.8**
Based on Anions   **4.4**
Target   **4.6**

Cs-137 (uCi/mL)	0.014	0.06163	4.4

AN102 small C	Feed	Concentrate	Conc.Factor
Na (Molar)	1.15	5.00	4.37
Na, mg/L	26326.88	114951.49	4.37
Cs-137 (uCi/mL)	0.014	0.062	4.40
Tc-99 (uCi/mL)	0.010	0.050	4.40

Table 8.10. Decontamination Factors Calculated from Evaporation of AN-102

Final Concentrations ICP-ES,mg/L	AN102 Feed Average		AN102 Condensate Average			Decontamination Factor	
Al	1432.8		0.071			2.0E+04	
Ba	652.6		0.0025			2.6E+05	
Cd	5.5	<	0.003		>	1.8E+03	
Cr	2.0	<	0.007		>	2.9E+02	
Cu	1.7	<	0.003		>	5.7E+02	
Ca	14.4		0.031			4.7E+02	
Fe	0.4		0.0055			7.5E+01	
Mg	0.1	<	0.001		>	1.0E+02	
Mo	5.3	<	0.006		>	8.8E+02	
Na	26326.9		0.316			8.3E+04	
Ni	32.0		0.01			3.2E+03	
Pb	11.5		0.0335			3.4E+02	
Si	58.8		0.26			2.3E+02	
Sr	0.6	<	0.001		>	6.2E+02	
Zn	2.7	<	0.003		>	9.1E+02	
	Average		**Average**				
K(AA), mg/L	209.5	<	0.135		>	1.6E+03	
Free OH, Molar	0.2	<	0.002		>	9.4E+01	
TIC, mg/L	415.0		in progress			#VALUE!	
TOC, mg/L	3304.0		in progress			#VALUE!	
Anions, mg/L	**Average**		**Average**				
Fluoride	158	<	0.2		>	7.9E+02	
Formate	1023	<	1		>	1.0E+03	
Chloride	284	<	0.2		>	1.4E+03	
Nitrite	6759	<	1		>	6.8E+03	
Nitrate	40330	<	1		>	4.0E+04	
Sulfate	35	<	0.5		>	7.0E+01	
Oxalate	120	<	1		>	1.2E+02	
Cs-137, uCi/mL	0.014	<	5.87E-06		>	2.4E+03	
Tc-99, uCi/mL	9.86E-03	<	1.42E-05		>	6.9E+02	

Waste Glass Formulation

Results of the AN-102 concentrate analyses (Table 8.6) were transmitted to the VSL to develop a glass recipe for the waste stream. The recipe uses a mixture of various minerals and added sugar as reductant. The specific amounts and type of minerals used in the formulation is considered proprietary to GTS Duratek/Vitreous State Laboratory and are thus not presented in this report. The target waste loading for the AN-102 glass formulation was nominally ~ 20 wt% Na_2O_2 per the original Test Specification.[1] Other major target elements shown as wt% metal oxides are shown in Table 8.11 below. The sulfur content of the glass formulated for this AN-102 sulfate pretreated waste is also shown to be targeted at a relatively low amount of 0.005 wt% as oxide, SO_3.

Table 8.11. Waste Loading Targets for AN-102 Glass Formulation.

Target AN-102 Glass	
Oxide	**Wt% (oxide)**
Al2O3	6.2
B2O3	9.0
CaO	2.0
Fe2O3	7.0
MgO	2.0
Na2O	20.0
SiO2	44.9
TiO2	2.0
ZnO	3.0
ZrO2	3.0
SO3	0.005

8.4   Conclusions

The experiments presented in this summary support concentration of a sulfate pretreated Env. C AN-102 decontaminated supernate. Evaporation testing in a reduced pressure, low temperature evaporator successfully produced a concentrated supernate that was formulated for a 20 wt% Na_2O_2 LAW glass. The evaporation showed no formation of solids after concentration by ~ 4.6X to within 80% of saturation. The condensate was shown to be decontaminated of major species Al, Na and Nitrate by a decontamination factor on the order of 2E+04 to 8E+04. Actual production of the targeted glass for this sulfate pretreated AN-102 stream was not pursued due to RPP project personnel decisions not to pursue sulfate pretreatment. The concentrated supernate was eventually returned to Hanford as a 'residue' stream.

8.5 Controls and Quality Assurance

QA and QC programs applied to the testing described in this technical report include SRTC procedures for control of measurement and testing equipment (M&TE), tracking of radioactive samples, control of laboratory notebooks, and routine ADS QA and QC.[7,8,9] The QA program applied by SRTC for preparation and analysis of the AN-102 glass sample complies with the requirements of NQA-1.

Analytic standards were required for all analyses performed for this study. Use of these standards is part of routine ADS QA and QC and are part of the procedures in Manual L16.1 for operating the analytical instruments.

All M&TE used to perform the evaporation and vitrification experiments was used within the specified calibration period. Calibrations were verified as required for each mass balance instrument. A record of the calibration was routinely maintained in the logbook designated for that piece of equipment.

All personnel who performed steps of the evaporation and vitrification testing were trained on the ITS procedure for operating the evaporation apparatus and furnace. In addition, they were trained on calibrating and operating equipment used in these steps. Training records were maintained for all personnel working on this project.

All laboratory data obtained in the tasks described in this technical report are included as permanent record in Charles L. Crawford's WSRC laboratory notebook: WSRC-NB-99-00182. Associated data to these two WSRC laboratory notebooks is also kept as permanent record in the three-ring binders labeled as: LAW Envelope C, Sample AN-102, Vitrification and Product Testing, Charles L. Crawford.

8.6 References

1. TWRS Privatization, Contract No. DE-AC27-96RL13308, Mod. No. A013, Section C: Statement of Work, 1998. (See http://www.hanford.gov/doe/contracts/de-ac06-96rl13308/sectionc-1.html)

2. Technical and Development Support to TWRS Design, K. A. Johnson and M. E. Johnson, K0104_077_PRC, December 1997.

3. Westinghouse Savannah River Company, "Work for Others Agreement," WFO-96-004, 1996; "Vitrification of Four Radioactive Hanford Waste Samples (U)", D. M. Ferrara, C. L. Crawford, B. C. Ha, N. E. Bibler and A. S. Choi, SRTC-BNFL-023, Rev. 2, January 5, 1998.

4. Westinghouse Savannah River Company, "Work for Others Agreement," WFO-98-003, 1998; RPP-WTP Development Task Specification, TS-W375LV-TE00006, Vitrification of LAW Envelope A Sample AN-103 and Product Testing, S. Arm (CHG) and G. Smith (Battelle).

5. Task Technical and Quality Assurance Plan for Bench Scale LAW Evaporation with Simulants", T. Bond Calloway, Jr. and D. P. Lambert, BNF-003-0056, Rev. 0, May 11, 1999; "Evaporation of Hanford Envelope B Simulant (AZ-101) Preliminary Report", T. B. Calloway, Jr., A. S. Choi and P. R. Monson, BNF-003-98-0166, January 6, 2000.

6. "Crucible-Scale Active Vitrification Testing Envelope A, Tank 241-AN-103 (U)", C. L. Crawford, D. M. Ferrara, R. F. Schumacher and N. E. Bibler, WSRC-TR-2000-00322, SRT-RPP-2000-00021, Formerly BNF-003-98-0237, Rev. 0, September 15, 2000.

Appendix 1

Attachment 1. Envelope B (AZ-101) Simulant Characterization

ADS#	300132861			
ICP-ES				
	mg/L	**Molarity**	**As-Prepared (M)**	**% of Target**
Al	8155	0.302	0.40	76
Cr	682	5.8769E-03	0.01	59
P	509	1.6435E-02	0.02	82
PM1	0.4	3.6436E-06	NA	
Si	3.5	1.2353E-04	NA	
S	3010	9.3869E-02	0.18	52
IC Anion				
F	1473	2.38E-02	0.10	24
Cl	210	5.92E-03	0.01	59
NO_2^-	59439	1.29	1.41	92
NO_3^-	71383	1.15	1.22	94
PO_4^{3-}	1386	1.46E-02	0.02	73
SO_4^{2-}	8327	8.67E-02	0.18	48
Formate	<100	---	0.00	---
Oxalate	<100	---	0.00	---
TIC	10662	---	4564	234
TOC	266	---	0.00	---

Attachment 2. Batch Contact Data for Pretreated Hanford Supernate

Sulfate				
Sample ID	**BNF-C310-S655**	**BNF-C310-S655**	**BNF-C310-SO4**	**BNF-C310-SO4**
	SO4-1	**SO4-1D**	**spike F-1**	**spike F-2**
LIMS #	300132926	300132952	300132953	300132954
solution Mass (g)	6.6858	6.1174	6.162	5.8527
resin vol (mL)	0.6	0.6	na	na
solution vol. (mL)	5.31	4.86	4.89	4.65
SO_4 conc. (ug/mL)	3654	3777	5298	4425
sample mass (g)	na	na	1.149	
SO4 removed (ug/mL)	1207.5	1084.5	na	
Kd (mL/g resin)	7.3	5.8	Avg.--->	6.56
% ave. R	23.6			
Temp.	26 deg. C			
contact time	24 h			

Attachment 3. Batch Contact Data for Envelope B Simulant

Sample #	SSIX-38-1	SSIX-38-1-D	SSIX-38-FD	
ADS #	300132858	300132859	300132860	
Solution Mass (g)	6.1037	6.1065	6.1060	
Resin Volume (mL)	0.6	0.6	---	
Solution Volume (mL)	4.96	4.96	4.96	
Temperature (°C)	22	22	22	
Shake Time	24.0 hrs	24.0 hrs	24.0 hrs	
				Average
IC Anion				**% Removal**
$[SO_4^{2-}]$ (mg/L)	6246	6316	8338	24.7
$[F^-]$ (mg/L)	1387	1379	1493	7.4
$[Cl^-]$ (mg/L)	185	189	206	9.2
$[NO_2^-]$ (mg/L)	50052	52407	58538	12.5
$[NO_3^-]$ (mg/L)	68084	70672	70251	1.2
$[PO_4^{3-}]$	1246	1200	1417	13.7
Formate	<100	<100	<100	---
Oxalate	<100	<100	<100	---
ICP-ES				
Al	7555	6805	7860	8.7
Cr	449	424	672	35.1
P	455	428	493	10.5
PM1	1.1	1.0	0.3	**---**
Si	3.4	3.0	3.3	2.9
S	2335	2175	2940	23.3

Attachment 4. Column Data for Pretreated Hanford Supernate

Sulfate IX column loading data									
		ADS	SO4	Cl	F	PO4	NO2	NO3	
Sample I.D		LIMS#s	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	
BNF-C310-SO4-Spike F-1		3-132953	5298	2606	86	469	40623	56360	
BNF-C310-SO4-Spike F-2		3-132954	4425	2647	88	513	41991	60129	
BNF-C310-S655-SO4-Cr3-eff-1		3-132927	71	42	20	100	554	55495	
BNF-C310-S655-SO4-Cr3-eff-3		3-132932	548	684	60	100	11556	56406	
BNF-C310-S655-SO4-Cr3-eff-5		3-132934	1804	1438	82	187	23720	58663	
BNF-C310-S655-SO4-Cr3-eff-7		3-132936	3427	1994	88	372	32202	57513	
BNF-C310-S655-SO4-Cr3-eff-9		3-132938	4328	2227	86	433	35334	57613	
BNF-C310-S655-SO4-Cr3-eff-11		3-132940	4725	2378	86	503	36969	58643	
BNF-C310-S655-SO4-Cr3-eff-13		3-132942	4869	2474	86	504	37615	56949	
BNF-C310-S655-SO4-Cr3-eff-15		3-132944	5053	2522	88	556	38782	57727	
BNF-C310-S655-SO4-Cr3-eff-17		3-132946	5186	2568	82	489	39858	56308	
BNF-C310-S655-SO4-Cr3-eff-19		3-132948	4870	2436	85	434	37379	54573	
BNF-C310-S655-SO4-Cr3-eff-composite		3-132950	3544	1950	84	329	31982	58236	
BNF-C310-S655-SO4-Cr3-NaOHwash-1		3-133120	4479	2712	90	546	42411	63429	
BNF-C310-S655-SO4-Cr3-NaOHwash-2		3-132951	4163	2155	93	386	34342	51667	
BNF-C310-S655-SO4-Cr3-NaNO3wash-1		3-133121	6.99E-01	2.22E-02	2647	1396	86	277	

Attachment 5. Column Data for Envelope B Simulant

Column Loading
IC Anion Data

	300132861	300132862	300132863	300132864	300132865	300132866	300132867	300132868	300132869	300132870
	SSIX-39-FD	SSIX-39-1	SSIX-39-2	SSIX-39-3	SSIX-39-4	SSIX-39-5	SSIX-39-6	SSIX-39-7	SSIX-39-8	SSIX-39-9
F (mg/L)	1473	<20	391	920	1143	1262	1318	1374	1391	1437
Formate	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Cl	210	<20	38	102	144	167	181	187	188	196
Nitrite	59439	<100	13034	35388	47385	52688	57048	54110	57935	53358
Nitrate	71383	544424	51330	62680	65111	64811	66200	66854	66790	66314
Phosphate	1386	<100	<100	467	855	1041	1168	1243	1289	1297
Sulfate	8327	<50	1185	3071	4661	5818	6633	6958	7010	7455
Oxalate	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
TIC	10662									
TOC	266									
		C/C_o	C/C_o	C/C_o	C/C_o	C/C_o	C/C_o	C/C_o	C/C_o	C/C_o
F		---	0.27	0.62	0.78	0.86	0.89	0.93	0.94	0.98
Cl		---	0.18	0.49	0.69	0.80	0.86	0.89	0.90	0.93
Nitrite		---	0.22	0.60	0.80	0.89	0.96	0.91	0.97	0.90
Nitrate		---	0.72	0.88	0.91	0.91	0.93	0.94	0.94	0.93
Phosphate		---	---	0.34	0.62	0.75	0.84	0.90	0.93	0.94
Sulfate		<0.006	0.14	0.37	0.56	0.70	0.80	0.84	0.84	0.90
CV		1	2	3	4	5	6	7	8	9

ICP-ES Data

	300132861	300132862	300132863	300132864	300132865	300132866	300132867	300132868	300132869	300132870
Al (mg/L)	8155	4.0	2065	4615	5850	6895	7625	7310	8490	7305
Cr	682	0.05	52	166	319	470	549	571	633	623
P	509	<0.9	70	221	310	394	444	450	480.5	466.5
PM1	0.4	361	2.3	1.9	2.1	2.4	2.4	2.3	2.2	2.1
Si	3.5	4.6	2.5	2.5	3.0	3.7	4.0	3.9	4.5	3.9
S	3010	<0.5	436	1080	1655	2210	2510	2605	2795	2750
Al C/C_o	NA	0.00	0.25	0.57	0.72	0.85	0.94	0.90	1.04	0.90
Cr C/C_o	NA	0.00	0.08	0.24	0.47	0.69	0.80	0.84	0.93	0.91
P C/C_o	NA		0.14	0.43	0.61	0.77	0.87	0.88	0.94	0.92
PM1 C/C_o	NA	901.25	5.68	4.83	5.14	5.88	6.06	5.69	5.40	5.33
Si C/C_o	NA	1.31	0.70	0.72	0.86	1.07	1.14	1.12	1.27	1.11
S C/C_o	NA		0.14	0.36	0.55	0.73	0.83	0.87	0.93	0.91
CV		1	2	3	4	5	6	7	8	9

Attachment 5. (cont.)

	Effluent Composite		**Column Wash Fractions**		
IC Anion Data					
	300132871	300132872	300132873	300132874	300132875
	SSIX-39-CP-EF	SSIX-39-W-1	SSIX-39-W-2	SSIX-39-W-3	SSIX-39-W-4
F (mg/L)	916	1438	1462	1008	538
Formate	<100	<100	<100	<100	<100
Cl	96	198	204	123	55
Nitrite	36533	54198	54935	41952	22415
Nitrate	54868	64821	65571	60833	40368
Phosphate	656	1313	1340	607	321
Sulfate	4804	7478	7741	5143	2678
Oxalate	<100	<100	<100	<100	<100
TIC	5440	8836	9006	6026	3876
TOC	572	204.3	<200	272	297
	C/C_o	C/C_o	C/C_o	C/C_o	C/C_o
F	0.62	0.98	0.99	0.68	0.37
Cl	0.46	0.94	0.97	0.59	0.26
Nitrite	0.61	0.91	0.92	0.71	0.38
Nitrate	0.77	0.91	0.92	0.85	0.57
Phosphate	0.47	0.95	0.97	0.44	0.23
Sulfate	0.58	0.90	0.93	0.62	0.32
ICP-ES Data					
Al (mg/L)	4795	7290	6985	4525	2510
Cr	332	629	630	379	208
P	271	504	474	266	147
PM1	2.2	2.1	2.0	1.8	1.4
Si	2.4	5.7	5.7	2.4	1.9
S	1535	2940	2975	1630	922
Al C/C_o	0.59	0.89	0.86	0.55	0.31
Cr C/C_o	0.49	0.92	0.92	0.56	0.31
P C/C_o	0.53	0.99	0.93	0.52	0.29
PM1 C/C_o	5.48	5.14	5.08	4.39	3.54
Si C/C_o	0.69	1.63	1.64	0.68	0.53
S C/C_o	0.51	0.98	0.99	0.54	0.31

Attachment 5. (cont.)

Column Elution

	300132876	300132877	300132878	300132879	300132880	300132881	300132882
IC Anion Data	SSIX-E-1	SSIX-E-2	SSIX-E-3	SSIX-E-4	SSIX-E-6	SSIX-E-8	SSIX-E-10
F (mg/L)	93	22	<20	<20	<20	<20	<20
Formate	<100	<100	<100	<100	<100	<100	<100
Cl	10	2	<20	<20	<20	<20	<20
Nitrite	4298	1042	<100	<100	<100	<100	<100
Nitrate	20087	17224	22009	25665	28117	28542	28834
Phosphate	<100	<100	<100	<100	<100	<100	<100
Sulfate	430	158	<50	<50	34	31	30
Oxalate	<100	<100	<100	<100	<100	<100	<100
TIC	453	269	<200	<200	<200	26	19
TOC	593	541	549	459	583	515	405
CV	1	2	3	4	6	8	10

	300132876	300132877	300132878	300132879	300132880	300132881	300132882
ICP-ES	SSIX-E-1	SSIX-E-2	SSIX-E-3	SSIX-E-4	SSIX-E-6	SSIX-E-8	SSIX-E-10
Al (mg/L)	593	145	64	24	7.1	1.4	3.6
Cr	37	28	89	100	76	39	24
P	42	23	55	44	12	3.7	1.5
PM1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Si	6.0	1.9	1.0	0.8	<0.6	<0.6	<0.6
S	189	74	12	12	14	13	12
CV	1	2	3	4	6	8	10
Cr C/Co	0.054	0.041	0.131	0.147	0.112	0.057	0.036
S C/Co	0.063	0.025	0.004	0.004	0.005	0.004	0.004

Attachment 5. (cont.)

	Eluate Composite	Post-Elution Wash		Post-Elution Wash Composite
	300132883	300132884	300132885	300132886
IC Anion Data	SSIX-E-CP	SSIX-E-W-1	SSIX-E-W-2	SSIX-W-CP
F (mg/L)	25	<20	<20	<20
Formate	<100	<100	<100	<100
Cl	<20	<20	<20	<20
Nitrite	<100	<100	<100	<100
Nitrate	26055	27672	27485	27561
Phosphate	<100	<100	<100	<100
Sulfate	134	27	25	24
Oxalate	<100	<100	<100	<100
TIC	22	<200	<200	<200
TOC	381	322	262	275
CV				

	300132883	300132884	300132885	300132886
ICP-ES Data	SSIX-E-CP	SSIX-E-W-1	SSIX-E-W-2	SSIX-W-CP
Al (mg/L)	324	0.7	0.4	0.6
Cr	54	16	15	16
P	10	1.0	0.9	1.4
PM1	<0.2	<0.2	<0.2	<0.2
Si	2.24	<0.6	<0.6	<0.6
S	76	12	11	10

Attachment 6. Column Elution Data for Envelope B Simulant

Column Elution

	300132876	300132877	300132878	300132879	300132880	300132881	300132882
IC Anion Data	SSIX-E-1	SSIX-E-2	SSIX-E-3	SSIX-E-4	SSIX-E-6	SSIX-E-8	SSIX-E-10
F (mg/L)	93	22	<20	<20	<20	<20	<20
Formate	<100	<100	<100	<100	<100	<100	<100
Cl	10	2	<20	<20	<20	<20	<20
Nitrite	4298	1042	<100	<100	<100	<100	<100
Nitrate	20087	17224	22009	25665	28117	28542	28834
Phosphate	<100	<100	<100	<100	<100	<100	<100
Sulfate	430	158	<50	<50	34	31	30
Oxalate	<100	<100	<100	<100	<100	<100	<100
TIC	453	269	<200	<200	<200	26	19
TOC	593	541	549	459	583	515	405
CV	1	2	3	4	6	8	10

	300132876	300132877	300132878	300132879	300132880	300132881	300132882
ICP-ES	SSIX-E-1	SSIX-E-2	SSIX-E-3	SSIX-E-4	SSIX-E-6	SSIX-E-8	SSIX-E-10
Al (mg/L)	593	145	64	24	7.1	1.4	3.6
Cr	37	28	89	100	76	39	24
P	42	23	55	44	12	3.7	1.5
PM1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Si	6.0	1.9	1.0	0.8	<0.6	<0.6	<0.6
S	189	74	12	12	14	13	12
CV	1	2	3	4	6	8	10
Cr C/Co	0.054	0.041	0.131	0.147	0.112	0.057	0.036
S C/Co	0.063	0.025	0.004	0.004	0.005	0.004	0.004

Attachment 6. Column Elution Data for Envelope B Simulant

	Eluate Composite	Post-Elution Wash		Post-Elution Wash Composite
	300132883	300132884	300132885	300132886
IC Anion Data	SSIX-E-CP	SSIX-E-W-1	SSIX-E-W-2	SSIX-W-CP
F (mg/L)	25	<20	<20	<20
Formate	<100	<100	<100	<100
Cl	<20	<20	<20	<20
Nitrite	<100	<100	<100	<100
Nitrate	26055	27672	27485	27561
Phosphate	<100	<100	<100	<100
Sulfate	134	27	25	24
Oxalate	<100	<100	<100	<100
TIC	22	<200	<200	<200
TOC	381	322	262	275
	300132883	300132884	300132885	300132886
ICP-ES Data	SSIX-E-CP	SSIX-E-W-1	SSIX-E-W-2	SSIX-W-CP
Al (mg/L)	324	0.7	0.4	0.6
Cr	54	16	15	16
P	10	1.0	0.9	1.4
PM1	<0.2	<0.2	<0.2	<0.2
Si	2.24	<0.6	<0.6	<0.6
S	76	12	11	10

Appendix 2

Table 1. Evaporation of 25 volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	25% Evaporation mg/L	25% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	11157	837	-3%
$[NO_3^-]$	68020	6802	94311	7073	-4%
$[NO_2^-]$	62439	6244	84751	6356	-2%
$[PO_4^{3-}]$	2377	238	3245	243	-2%
$[Cl^-]$	175	18	186	14	20%
$[F^-]$	976	98	962	72	26%

Table 2. Evaporation of 50 volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	50% Evaporation mg/L	50% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	2238	112	86%
$[NO_3^-]$	68020	6802	183267	9163	-35%
$[NO_2^-]$	62439	6244	156872	7844	-26%
$[PO_4^{3-}]$	2377	238	704	35	85%
$[Cl^-]$	175	18	270	14	23%
$[F^-]$	976	98	<20	1	>99%

Table 3. Addition of Lime followed by Evaporation of 25 Volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	25% Evaporation mg/L	25% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	6793	509	37%
$[NO_3^-]$	68020	6802	102472	7685	-13%
$[NO_2^-]$	62439	6244	92471	6935	-11%
$[PO_4^{3-}]$	2377	238	3448	259	-9%
$[Cl^-]$	175	18	194	15	17%
$[F^-]$	976	98	<384	29	70%

Table 4. Addition of Lime followed by Evaporation of 50 Volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	50% Evaporation mg/L	50% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	4967	248	69%
$[NO_3^-]$	68020	6802	167273	8364	-23%
$[NO_2^-]$	62439	6244	145425	7271	-16%
$[PO_4^{3-}]$	2377	238	658	33	86%
$[Cl^-]$	175	18	260	13	26%
$[F^-]$	976	98	<20	1	99%

Table 5. Addition of Solid $Ca(OH)_2$ to an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	0% Evaporation mg/L	0% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	6952	695	14%
$[NO_3^-]$	68020	6802	136151	13615	-100%
$[NO_2^-]$	62439	6244	121143	12114	-94%
$[PO_4^{3-}]$	2377	238	92	9	96%
$[Cl^-]$	175	18	212	21	-21%
$[F^-]$	976	98	<20	2	98%

Table 6. Addition of Solid $Ca(OH)_2$ followed by Evaporation of 20 Volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	20% Evaporation mg/L	20% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	10029	802	1%
$[NO_3^-]$	68020	6802	85546	6844	-1%
$[NO_2^-]$	62439	6244	78243	6259	0%
$[PO_4^{3-}]$	2377	238	807	65	73%
$[Cl^-]$	175	18	159	13	27%
$[F^-]$	976	98	468	37	62%

Table 7. Addition of Solid Ca(OH)₂ followed by Evaporation of 40 Volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	40% Evaporation mg/L	40% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	11464	688	15%
$[NO_3^-]$	68020	6802	120905	7254	-7%
$[NO_2^-]$	62439	6244	108429	6506	-4%
$[PO_4^{3-}]$	2377	238	456	27	88%
$[Cl^-]$	175	18	202	12	31%
$[F^-]$	976	98	137	8	92%

Table 8. Addition of Solid Ca(OH)₂ followed by Evaporation of 50 Volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	50% Evaporation mg/L	50% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	7957	398	51%
$[NO_3^-]$	68020	6802	66676	3334	51%
$[NO_2^-]$	62439	6244	62111	3106	50%
$[PO_4^{3-}]$	2377	238	2153	108	55%
$[Cl^-]$	175	18	171	9	51%
$[F^-]$	976	98	898	45	54%

Table 9. Addition of Solid SrCl₂ to an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	0% Evaporation mg/L	0% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	8019	802	1%
$[NO_3^-]$	68020	6802	69073	6907	-2%
$[NO_2^-]$	62439	6244	63791	6379	-2%
$[PO_4^{3-}]$	2377	238	2116	212	11%
$[Cl^-]$	175	18	4300	430	-2357%
$[F^-]$	976	98	712	71	27%

Table 10. Addition of Solid SrCl₂ followed by Evaporation of 30 Volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	30% Evaporation mg/L	30% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	9220	645	21%
$[NO_3^-]$	68020	6802	103300	7231	-6%
$[NO_2^-]$	62439	6244	93900	6573	-5%
$[PO_4^{3-}]$	2377	238	3173	222	7%
$[Cl^-]$	175	18	13166	922	-5166%
$[F^-]$	976	98	1890	132	-36%

Table 11. Addition of Solid SrCl₂ followed by Evaporation of 50 Volume Percent of 100 mL of an Envelope B Simulant (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	50% Evaporation mg/L	50% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	5817	291	64%
$[NO_3^-]$	68020	6802	150611	7531	-11%
$[NO_2^-]$	62439	6244	133204	6660	-7%
$[PO_4^{3-}]$	2377	238	4144	207	13%
$[Cl^-]$	175	18	19035	952	-5339%
$[F^-]$	976	98	1106	55	43%

Table 12. Addition of 5.0 mL of a 2.0 M SrCl₂ Solution to 100 mL of an Envelope B Simulant. (Table 4.2 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	0% Evaporation mg/L	0% Evaporation mg	% Removed
$[SO_4^{2-}]$	8120	812	5694	569	30%
$[NO_3^-]$	68020	6802	49946	4995	27%
$[NO_2^-]$	62439	6244	46865	4687	25%
$[PO_4^{3-}]$	2377	238	330	33	86%
$[Cl^-]$	175	18	10478	1048	-5887%
$[F^-]$	976	98	660	66	32%

Table 13. Evaporation of 20 volume Percent of 25 mL of an Envelope B Simulant (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	396	17567	351	11%
$[NO_3^-]$	59796	1495	84314	1686	-13%
$[NO_2^-]$	60515	1513	84299	1686	-11%
$[PO_4^{3-}]$	1855	46	2534	51	-9%
$[Cl^-]$	161	4	176	4	13%
$[F^-]$	843	21	465	9	56%
Al	7965	199	10700	214	-7%
Cr	677	17	901	18	-6%
Na	92000	2300	117000	2340	-2%
P	748	19	997	20	-7%
S	6325	158	7015	140	11%
K	4350	109	5530	111	-2%

Table 14. Evaporation of 30 volume Percent of 25 mL of an Envelope B Simulant (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	396	15780	276	30%
$[NO_3^-]$	59796	1495	96553	1690	-13%
$[NO_2^-]$	60515	1513	96168	1683	-11%
$[PO_4^{3-}]$	1855	46	2753	48	-4%
$[Cl^-]$	161	4	175	3	24%
$[F^-]$	843	21	116	2	90%
Al	7965	199	11850	207	-4%
Cr	677	17	980	17	-1%
Na	92000	2300	122500	2144	7%
P	748	19	1083	19	-1%
S	6325	158	6145	108	32%
K	4350	109	6220	109	0%

Table 15. Evaporation of 40 volume Percent of 25 mL of an Envelope B Simulant (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	396	14717	221	44%
$[NO_3^-]$	59796	1495	96504	1448	3%
$[NO_2^-]$	60515	1513	97399	1461	3%
$[PO_4^{3-}]$	1855	46	2703	41	13%
$[Cl^-]$	161	4	288	4	-7%
$[F^-]$	843	21	582	9	59%
Al	7965	199	12250	184	8%
Cr	677	17	1017	15	10%
Na	92000	2300	128000	1920	17%
P	748	19	1130	17	9%
S	6325	158	5775	87	45%
K	4350	109	6300	95	13%

Table 16. Evaporation of 50 volume Percent of 25 mL of an Envelope B Simulant (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	396	14228	178	55%
$[NO_3^-]$	59796	1495	107270	1341	10%
$[NO_2^-]$	60515	1513	107345	1342	11%
$[PO_4^{3-}]$	1855	46	2280	29	39%
$[Cl^-]$	161	4	<20	<0.25	>94%
$[F^-]$	843	21	<20	<0.25	>99%
Al	7965	199	13950	174	12%
Cr	677	17	1123	14	17%
Na	92000	2300	142000	1775	23%
P	748	19	1070	13	28%
S	6325	158	5570	70	56%
K	4350	109	7290	91	16%

Table 17. Evaporation of 60 volume Percent of 25 mL of an Envelope B Simulant (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	396	11379	114	71%
$[NO_3^-]$	59796	1495	118272	1183	21%
$[NO_2^-]$	60515	1513	117806	1178	22%
$[PO_4^{3-}]$	1855	46	1492	15	68%
$[Cl^-]$	161	4	350	4	13%
$[F^-]$	843	21	293	3	86%
Al	7965	199	14650	147	26%
Cr	677	17	1243	12	27%
Na	92000	2300	149500	1495	35%
P	748	19	857	9	54%
S	6325	158	4850	49	69%
K	4350	109	7810	78	28%

Table 18. Addition of 1.5 mL of a 3.0 M $Sr(NO_3)_2$ Solution to 25 mL of an Envelope B Simulant followed by Evaporation of 30 Volume Percent of the Mixture. (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	396	13896	243	39%
$[NO_3^-]$	59796	1495	108903	1906	-27%
$[NO_2^-]$	60515	1513	82056	1436	5%
$[PO_4^{3-}]$	1855	46	2466	43	7%
$[Cl^-]$	161	4	157	3	32%
$[F^-]$	843	21	156	3	87%
Al	7965	199	10300	180	9%
Cr	677	17	865	15	11%
Na	92000	2300	110000	1925	16%
P	748	19	930	16	13%
S	6325	158	5520	97	39%
K	4350	109	5300	93	15%

Table 19. Addition of 1.5 mL of a 3.0 M Sr(NO₃)₂ Solution to 25 mL of an Envelope B Simulant followed by Evaporation of 50 Volume Percent of the Mixture. (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	15836	396	15764	197	50%
[NO₃⁻]	59796	1495	160391	2005	-34%
[NO₂⁻]	60515	1513	118135	1477	2%
[PO₄³⁻]	1855	46	2972	37	20%
[Cl⁻]	161	4	321	4	0%
[F⁻]	843	21	279	3	83%
Al	7965	199	14100	176	11%
Cr	677	17	1130	14	17%
Na	92000	2300	139500	1744	24%
P	748	19	1160	15	22%
S	6325	158	5700	71	55%
K	4350	109	7540	94	13%

Table 20. Addition of 2.5 mL of a 2.0 M SrCl₂ Solution to 25 mL of an Envelope B Simulant followed by Evaporation of 30 Volume Percent of the Mixture. (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	15836	396	12427	217	45%
[NO₃⁻]	59796	1495	66050	1156	23%
[NO₂⁻]	60515	1513	67079	1174	22%
[PO₄³⁻]	1855	46	1909	33	28%
[Cl⁻]	161	4	10072	176	-4279%
[F⁻]	843	21	289	5	76%
Al	7965	199	9090	159	20%
Cr	677	17	750	13	22%
Na	92000	2300	97000	1698	26%
P	748	19	781	14	27%
S	6325	158	5210	91	42%
K	4350	109	4700	82	24%

Table 21. Addition of 2.5 mL of a 2.0 M SrCl₂ Solution to 25 mL of an Envelope B Simulant followed by Evaporation of 50 Volume Percent of the Mixture. (Table 4.3 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	396	12973	162	59%
$[NO_3^-]$	59796	1495	96147	1202	20%
$[NO_2^-]$	60515	1513	96703	1209	20%
$[PO_4^{3-}]$	1855	46	2028	25	45%
$[Cl^-]$	161	4	15010	188	-4561%
$[F^-]$	843	21	<20.00	<0.25	>99%
Al	7965	199	12250	153	23%
Cr	677	17	1017	13	25%
Na	92000	2300	127000	1588	31%
P	748	19	1093	14	27%
S	6325	158	5200	65	59%
K	4350	109	6400	80	26%

Table 22. Addition of 0.5 mL of a 5.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 0.47:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	20246	506	19515	498	2%
$[NO_3^-]$	58184	1455	64556	1646	-13%
$[NO_2^-]$	54009	1350	53566	1366	-1%
$[PO_4^{3-}]$	2135	53	1819	46	13%
$[Cl^-]$	181	5	159	4	10%
$[F^-]$	898	22	782	20	11%
Al	7560	189	7270	185	2%
Ca	10	0.3	19	0.5	-94%
Cr	640	16	626	16	0%
Na	98400	2460	96700	2466	0%
P	740	19	663	17	9%
S	7260	182	7010	179	2%

117

Table 23. Addition of 1.0 mL of a 5.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 0.95:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	20246	506	17993	468	8%
$[NO_3^-]$	58184	1455	71867	1869	-28%
$[NO_2^-]$	54009	1350	50361	1309	3%
$[PO_4^{3-}]$	2135	53	1149	30	44%
$[Cl^-]$	181	4.53	144	3.74	17%
$[F^-]$	898	22	533	14	38%
Al	7560	189	6410	167	12%
Ca	10	0.25	6.20	0.16	36%
Cr	640	16	571	15	7%
Na	98400	2460	91300	2374	4%
P	740	19	428	11	40%
S	7260	182	6380	166	9%

Table 24. Addition of 1.5 mL of a 5.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 1.42:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	20246	506	18146	481	5%
$[NO_3^-]$	58184	1455	77666	2058	-41%
$[NO_2^-]$	54009	1350	51356	1361	-1%
$[PO_4^{3-}]$	2135	53	893	24	56%
$[Cl^-]$	181	4.53	164	4.35	4%
$[F^-]$	898	22	366	10	57%
Al	7560	189	3940	104	45%
Ca	10	0.25	<2.0	<0.05	>79%
Cr	640	16	617	16	-2%
Na	98400	2460	94700	2510	-2%
P	740	19	365	10	48%
S	7260	182	6750	179	1%

Table 25. Addition of 2.0 mL of a 5.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 1.90:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	20246	506	16418	443	12%
[NO₃⁻]	58184	1455	90560	2445	-68%
[NO₂⁻]	54009	1350	50611	1366	-1%
[PO₄³⁻]	2135	53	270	7.29	86%
[Cl⁻]	181	4.53	123	3.32	27%
[F⁻]	898	22	159	4.29	81%
Al	7560	189	4170	113	40%
Ca	10	0.25	<2.0	<0.05	>78%
Cr	640	16	572	15	3%
Na	98400	2460	95100	2568	-4%
P	740	19	114	3.08	83%
S	7260	182	6040	163	10%

Table 26. Addition of 2.5 mL of a 5.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 2.37:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	20246	506	15350	422	17%
[NO₃⁻]	58184	1455	99468	2735	-88%
[NO₂⁻]	54009	1350	49872	1371	-2%
[PO₄³⁻]	2135	53	113	3.11	94%
[Cl⁻]	181	4.53	121	3.33	26%
[F⁻]	898	22	129	3.55	84%
Al	7560	189	2860	79	58%
Ca	10	0.25	<2.0	<0.06	>78%
Cr	640	16	564	16	3%
Na	98400	2460	92700	2549	-4%
P	740	19	52	1.43	92%
S	7260	182	5720	157	13%

Table 27. Addition of 3.0 mL of a 5.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 2.85:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	20246	506	13769	386	24%
$[NO_3^-]$	58184	1455	104997	2940	-102%
$[NO_2^-]$	54009	1350	49341	1382	-2%
$[PO_4^{3-}]$	2135	53	84	2.35	96%
$[Cl^-]$	181	4.53	116	3.25	28%
$[F^-]$	898	22	87	2.44	89%
Al	7560	189	2350	66	65%
Ca	10	0.25	<2.0	<0.06	>78%
Cr	640	16	537	15	6%
Na	98400	2460	90600	2537	-3%
P	740	19	38	1.06	94%
S	7260	182	5270	148	19%

Table 28. Addition of 5.0 mL of a 5.0 M Ca(NO₃)₂ Solution to 50 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 4.75:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	20246	1012	7283	437	57%
$[NO_3^-]$	58184	2909	133512	8011	-175%
$[NO_2^-]$	54009	2700	48892	2934	-9%
$[PO_4^{3-}]$	2135	107	<100.0	<6.00	>94%
$[Cl^-]$	181	9.05	107	6.42	29%
$[F^-]$	898	45	64	3.84	91%
Al	7560	378	674	40	89%
Ca	10	0.5	2.7	0.16	68%
Cr	640	32	439	26	18%
Na	98400	4920	87100	5226	-6%
P	740	37	<9.0	<0.54	>99%
S	7260	363	2970	178	51%

Table 29. Addition of 15.0 mL of a 5.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Calcium to Sulfate Molar Ratio of 14.2:1 (Table 4.4 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	20274	507	18	0.72	100%
[NO₃⁻]	57278	1432	246752	9870	-589%
[NO₂⁻]	56283	1407	38138	1526	-8%
[PO₄³⁻]	2119	53	<100	<4.0	>92%
[Cl⁻]	196	4.90	<100	<4.0	>18%
[F⁻]	797	20	<20	<0.8	>96%

Table 30. Addition of 0.5 mL of a 2.3 M Sr(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Strontium to Sulfate Molar Ratio of 0.22:1 (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	19842	496	19347	493	1%
[NO₃⁻]	56595	1415	58839	1500	-6%
[NO₂⁻]	53356	1334	50267	1282	4%
[PO₄³⁻]	2163	54	1521	39	28%
[Cl⁻]	223	6	232	6	-6%
[F⁻]	813	20	654	17	18%

Table 31. Addition of 1.0 mL of a 2.3 M Sr(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Strontium to Sulfate Molar Ratio of 0.44:1 (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	19842	496	18789	489	2%
[NO₃⁻]	56595	1415	64967	1689	-19%
[NO₂⁻]	53356	1334	51497	1339	0%
[PO₄³⁻]	2163	54	1108	29	47%
[Cl⁻]	223	6	231	6	-8%
[F⁻]	813	20	474	12	39%

Table 32. Addition of 2.0 mL of a 2.3 M Sr(NO$_3$)$_2$ Solution to 25 mL of an Envelope B Simulant. Strontium to Sulfate Molar Ratio of 0.88:1 (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	19842	496	18569	501	-1%
[NO$_3^-$]	56595	1415	71665	1935	-37%
[NO$_2^-$]	53356	1334	50231	1356	-2%
[PO$_4^{3-}$]	2163	54	1018	27	49%
[Cl$^-$]	223	6	190	5	8%
[F$^-$]	813	20	236	6	69%

Table 33. Addition of 3.0 mL of a 2.3 M Sr(NO$_3$)$_2$ Solution to 25 mL of an Envelope B Simulant. Strontium to Sulfate Molar Ratio of 1.32:1 (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	19842	496	17357	486	2%
[NO$_3^-$]	56595	1415	78414	2196	-55%
[NO$_2^-$]	53356	1334	47607	1333	0%
[PO$_4^{3-}$]	2163	54	535	15	72%
[Cl$^-$]	223	6	184	5	8%
[F$^-$]	813	20	92	3	87%

Table 34. Addition of 4.0 mL of a 2.3 M Sr(NO$_3$)$_2$ Solution to 25 mL of an Envelope B Simulant. Strontium to Sulfate Molar Ratio of 1.76:1 (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	19842	496	16311	473	5%
[NO$_3^-$]	56595	1415	83598	2424	-71%
[NO$_2^-$]	53356	1334	45088	1308	2%
[PO$_4^{3-}$]	2163	54	279	8	85%
[Cl$^-$]	223	6	156	5	19%
[F$^-$]	813	20	25	1	96%

Table 35. Addition of 5.0 mL of a 2.3 M Sr(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Strontium to Sulfate Molar Ratio of 2.20:1 (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	19842	496	15355	461	7%
$[NO_3^-]$	56595	1415	90279	2708	-91%
$[NO_2^-]$	53356	1334	44383	1331	0%
$[PO_4^{3-}]$	2163	54	67	2	96%
$[Cl^-]$	223	6	132	4	29%
$[F^-]$	813	20	17	1	97%

Table 36. Addition of 3.0 mL of a 2.3 M Sr(NO₃)₂ Solution to 25 mL of an Envelope B Simulant at 95°C. Strontium to Sulfate Molar Ratio of 1.32:1   (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	19842	496	23984	496	0%
$[NO_3^-]$	56595	1415	107576	2227	-57%
$[NO_2^-]$	53356	1334	64704	1339	0%
$[PO_4^{3-}]$	2163	54	1445	30	45%
$[Cl^-]$	223	6	156	3	42%
$[F^-]$	813	20	651	13	34%

Table 37. Addition of 15.0 mL of a 2.3 M Sr(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Strontium to Sulfate Molar Ratio of 6.8:1 (Table 4.5 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	20274	507	942	38	93%
$[NO_3^-]$	57278	1432	140368	5615	-292%
$[NO_2^-]$	56283	1407	37602	1504	-7%
$[PO_4^{3-}]$	2119	53	<100	4	92%
$[Cl^-]$	196	5	<100	4	18%
$[F^-]$	797	20	<20	1	96%

Table 38. Addition of 5.0 mL of a 0.15 M Ba(NO₃)₂ Solution to 25 mL of an Envelope A Simulant. Barium to Sulfate Molar Ratio of 1.1:1 (Table 4.7 in Report)

	Envelope A Simulant mg/L	Envelope A Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	2546	64	1577	47	26%
$[NO_3^-]$	93601	2340	81789	2454	-5%
$[NO_2^-]$	55505	1388	49091	1473	-6%
$[PO_4^{3-}]$	905	23	655	20	13%
$[Cl^-]$	4275	107	3644	109	-2%
$[F^-]$	536	13	445	13	0%
Al	11050	276	9165	275	0%
Cr	544	14	87	3	81%
Na	103500	2588	88400	2652	-2%
P	368	9	240	7	22%
S	929	23	561	17	28%
Ba	<0.50	<0.013	6	0.18	-1340%
Ca	47.0	1.2	0.6	0.02	98%

Table 39. Results of the TCLP on the Washed Precipitate from Table 38.

	TCLP Leachate Concentration mg/L
Ba	309
Ca	38
Cd	<0.28
Cr	3.37
Pb	<0.56
S	10.12

Table 40. Addition of 10.0 mL of a 0.2 M Ba(NO₃)₂ Solution to 25 mL of an Envelope A Simulant. Barium to Sulfate Molar Ratio of 3.3:1 (Table 4.7 in Report)

	Envelope A Simulant mg/L	Envelope A Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	2546	64	788	28	57%
$[NO_3^-]$	93601	2340	75351	2637	-13%
$[NO_2^-]$	55505	1388	42388	1484	-7%
$[PO_4^{3-}]$	905	23	519	18	20%
$[Cl^-]$	4275	107	3265	114	-7%
$[F^-]$	536	13	351	12	8%
Al	11050	276	7735	271	2%
Cr	544	14	51	2	87%
Na	103500	2588	75200	2632	-2%
P	368	9	158	6	40%
S	929	23	273	10	59%
Ba	<0.50	<0.013	7.5	0.26	-2000%
Ca	47.0	1.2	<0.2	0.01	99%

Table 41. Results of the TCLP on the Washed Precipitate from Table 40.

	Leachate Concentration mg/L
Ba	303
Ca	61
Cd	<0.18
Cr	0.32
Pb	<0.36
S	5.34

Table 42. Addition of 15.0 mL of a 0.2 M Ba(NO₃)₂ Solution to 25 mL of an Envelope A Simulant. Barium to Sulfate Molar Ratio of 5.5:1 (Table 4.7 in Report)

	Envelope A Simulant mg/L	Envelope A Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	2546	64	480	19	70%
[NO$_3^-$]	93601	2340	67731	2709	-16%
[NO$_2^-$]	55505	1388	36151	1446	-4%
[PO$_4^{3-}$]	905	23	361	14	36%
[Cl$^-$]	4275	107	2905	116	-9%
[F$^-$]	536	13	301	12	10%
Al	11050	276	6605	264	4%
Cr	544	14	15	1	96%
Na	103500	2588	64050	2562	1%
P	368	9	89	4	61%
S	929	23	157	6	73%
Ba	<0.50	<0.013	12	0.48	-3740%
Ca	47.0	1.2	<0.2	0.01	99%

Table 43. Results of the TCLP on the Washed Precipitate from Table 42.

	Leachate Concentration mg/L
Ba	5767
Ca	45
Cd	15.8
Cr	0.13
Pb	<0.27
S	1.60

Table 44. Addition of 0.184 g of Solid Ba(NO$_3$)$_2$ to 25 mL of an Envelope A Simulant at 60°C. Barium to Sulfate Molar Ratio of 0.8:1 (Table 4.7 in Report)

	Envelope A Simulant mg/L	Envelope A Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4$$^{2-}$]	3556	89	2897	72	19%
[NO$_3$$^-$]	93986	2350	99096	2477	-5%
[NO$_2$$^-$]	56002	1400	57227	1431	-2%
[PO$_4$$^{3-}$]	2874	72	2916	73	-1%
[Cl$^-$]	4441	111	4554	114	-3%
[F$^-$]	510	13	515	13	-1%
Al	11550	289	11850	296	-3%
Cr	578	14	212	5	63%
Na	97550	2439	102500	2563	-5%
P	356	9	338	8	5%
S	947	24	642	16	32%
Ba	27	0.68	11.2	0.28	59%

Table 45. Addition of 3.0 mL of a 0.2 M Ba(NO$_3$)$_2$ Solution to 25 mL of an Envelope A Simulant at 60°C. Barium to Sulfate Molar Ratio of 0.81:1 (Table 4.7 in Report)

	Envelope A Simulant mg/L	Envelope A Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4$$^{2-}$]	3556	89	2513	63	29%
[NO$_3$$^-$]	93986	2350	94505	2363	-1%
[NO$_2$$^-$]	56002	1400	54319	1358	3%
[PO$_4$$^{3-}$]	2874	72	2825	71	2%
[Cl$^-$]	4441	111	4378	109	1%
[F$^-$]	510	13	464	12	9%
Al	11550	289	11350	284	2%
Cr	578	14	127	3	78%
Na	97550	2439	95900	2398	2%
P	356	9	302	8	15%
S	947	24	462	12	51%
Ba	27	0.68	6.4	0.16	76%

Table 46. Addition of 0.3 mL of a 6.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope A Simulant followed by the Addition of 3.0 mL of 0.2 M Ba(NO₃)₂ Solution. Barium to Sulfate Molar Ratio of 0.85:1 (Table 4.7 in Report)

	Envelope A Simulant mg/L	Envelope A Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	3177	79	1073	30	62%
$[NO_3^-]$	90566	2264	80341	2274	0%
$[NO_2^-]$	54770	1369	42011	1189	13%
$[PO_4^{3-}]$	2330	58	567	16	72%
$[Cl^-]$	4115	103	3389	96	7%
$[F^-]$	552	14	119	3	76%
Al	11100	278	8490	240	13%
Cr	544	14	97	3	80%
Na	105500	2638	84200	2383	10%
P	372	9	223	6	32%
S	941	24	428	12	49%
Ba	0.7	0	49	1.39	-59930%
Ca	49.0	1.2	2.5	0.07	94%

Table 47. Results of the TCLP on the Washed Precipitate from Table 46.

	Leachate Concentration mg/L
Ba	545
Ca	26
Cd	<0.09
Cr	0.91
Pb	<2.27
S	<2.27

Table 48. Addition of 10.0 mL of a 0.2 M Ba(NO$_3$)$_2$ Solution to 10 mL of an Envelope B Simulant. Barium to Sulfate Molar Ratio of 1.2:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	15836	158	1102	22	86%
[NO$_3^-$]	59796	598	53055	1061	-77%
[NO$_2^-$]	60515	605	33144	663	-10%
[PO$_4^{3-}$]	1855	19	544	11	41%
[Cl$^-$]	161	1.6	93	1.9	-16%
[F$^-$]	843	8.4	659	13	-56%
Al	7965	80	3995	80	0%
Cr	677	6.8	25	0.5	93%
Na	92000	920	46350	927	-1%
P	748	7.5	243	4.9	35%
S	6325	63	440	8.8	86%
K	4350	44	2140	43	2%

Table 49. Addition of 15.0 mL of a 0.3 M Ba(NO$_3$)$_2$ Solution to 25 mL of an Envelope B Simulant. Barium to Sulfate Molar Ratio of 1.1:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	16779	419	1684	67	84%
[NO$_3^-$]	72583	1815	60745	2430	-34%
[NO$_2^-$]	61841	1546	40956	1638	-6%
[PO$_4^{3-}$]	1213	30	649	26	14%
[Cl$^-$]	305	7.6	204	8.2	-7%
[F$^-$]	859	21	677	27	-26%
Al	7530	188	4765	191	-1%
Cr	644	16	34	1.4	92%
Na	105000	2625	65300	2612	0%
P	501	13	230	9.2	27%
S	5960	149	610	24	84%
Ca	21.0	0.5	0.8	0.03	94%

Table 50. Results of the TCLP on the Washed Precipitate from Table 49.

	Leachate Concentration mg/L
Ba	340
Ca	7.6
Cd	<0.05
Cr	0.09
Pb	<0.10
S	2.30

Table 51. Addition of 30.0 mL of a 0.2 M Ba(NO₃)₂ Solution to 10 mL of an Envelope B Simulant. Barium to Sulfate Molar Ratio of 3.7:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	158	135	5.4	97%
$[NO_3^-]$	59796	598	36534	1461	-144%
$[NO_2^-]$	60515	605	15649	626	-3%
$[PO_4^{3-}]$	1855	19	29	1.2	94%
$[Cl^-]$	161	1.6	41	1.6	-2%
$[F^-]$	843	8.4	387	15	-84%
Al	7965	80	1835	73	8%
Cr	677	6.8	2.1	0.1	99%
Na	92000	920	21850	874	5%
P	748	7.5	15	0.6	92%
S	6325	63	43	1.7	97%
K	4350	44	1030	41	5%

Table 52. Addition of 45.0 mL of a 0.3 M Ba(NO₃)₂ Solution to 25 mL of an Envelope B Simulant. Barium to Sulfate Molar Ratio of 3.2:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	16779	419	439	31	93%
$[NO_3^-]$	72583	1815	51905	3633	-100%
$[NO_2^-]$	61841	1546	23358	1635	-6%
$[PO_4^{3-}]$	1213	30	244	17	44%
$[Cl^-]$	305	7.6	152	11	-40%
$[F^-]$	859	21	479	34	-56%
Al	7530	188	2685	188	0%
Cr	644	16	7.6	0.5	97%
Na	105000	2625	38100	2667	-2%
P	501	13	34	2.4	81%
S	5960	149	139	10	93%
Ca	21.0	0.5	<0.20	0.01	97%

Table 53. Results of the TCLP on the Washed Precipitate from Table 52.

	Leachate Concentration mg/L
Ba	1529
Ca	8.8
Cd	<0.05
Cr	0.02
Pb	<0.10
S	0.30

Table 54. Addition of 75.0 mL of a 0.3 M Ba(NO$_3$)$_2$ Solution to 25 mL of an Envelope B Simulant. Barium to Sulfate Molar Ratio of 5.3:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	16779	419	129	13	97%
[NO$_3^-$]	72583	1815	47987	4799	-164%
[NO$_2^-$]	61841	1546	16365	1637	-6%
[PO$_4^{3-}$]	1213	30	<100	<10.00	>67%
[Cl$^-$]	305	7.6	133	13	-74%
[F$^-$]	859	21	192	19	11%
Al	7530	188	1955	196	-4%
Cr	644	16	0.05	0.01	100%
Na	105000	2625	27350	2735	-4%
P	501	13	0.1	0.01	100%
S	5960	149	1.0	0.1	100%
Ca	21.0	0.5	<0.20	<0.02	>96%

Table 55. Results of the TCLP on the Washed Precipitate from Table 54.

	Leachate Concentration mg/L
Ba	1363
Ca	8.6
Cd	<0.05
Cr	0.02
Pb	<0.10
S	0.30

Table 56. Addition of 6.3 mL of a 0.7 M Ba(NO₃)₂ Solution at 60°C to 25 mL of an Envelope B Simulant at 60°C. Barium to Sulfate Molar Ratio of 1.0:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	16652	416	5211	130	69%
$[NO_3^-]$	72762	1819	86022	2151	-18%
$[NO_2^-]$	61732	1543	57678	1442	7%
$[PO_4^{3-}]$	2936	73	3174	79	-8%
$[Cl^-]$	1417	35	1432	36	-1%
$[F^-]$	1718	43	1665	42	3%
Al	8095	202	7490	187	7%
Cr	669	17	114	2.9	83%
Na	99350	2484	91650	2291	8%
P	472	12	549	14	-16%
S	6200	155	1695	42	73%

Table 57. Addition of 0.52g of Solid Ba(NO₃)₂ to 10 mL of an Envelope B Simulant. Barium to Sulfate Molar Ratio of 1.0:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	15836	158	9517	95	40%
$[NO_3^-]$	59796	598	74678	747	-25%
$[NO_2^-]$	60515	605	62210	622	-3%
$[PO_4^{3-}]$	1855	19	1674	17	10%
$[Cl^-]$	161	1.6	149	1.5	7%
$[F^-]$	843	8.4	870	8.7	-3%
Al	7965	80	7725	77	3%
Cr	677	6.8	320	3.2	53%
Na	92000	920	88300	883	4%
P	748	7.5	654	6.5	13%
S	6325	63	3595	36	43%
K	4350	44	4230	42	3%

Table 58. Addition of 0.69 g of Solid Ba(NO$_3$)$_2$ to 15 mL of an Envelope B Simulant. Barium to Sulfate Molar Ratio of 1.0:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	16652	250	5993	90	64%
[NO$_3^-$]	72762	1091	90414	1356	-24%
[NO$_2^-$]	61732	926	62049	931	-1%
[PO$_4^{3-}$]	2936	44	3288	49	-12%
[Cl$^-$]	1417	21	1456	22	-3%
[F$^-$]	1718	26	1602	24	7%
Al	8095	121	8045	121	1%
Cr	669	10	101	1.5	85%
Na	99350	1490	97000	1455	2%
P	472	7.1	634	10	-34%
S	6200	93	2040	31	67%

Table 59. Addition of 1.6 mL of a 6.0 M Ca(NO$_3$)$_2$ Solution to 25 mL of an Envelope B Simulant followed by the Addition of 15.0 mL of 0.3 M Ba(NO$_3$)$_2$ Solution. Barium to Sulfate Molar Ratio of 1.1:1 (Table 4.8 in Report)

	Envelope B Simulant mg/L	Envelope B Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO$_4^{2-}$]	16651	416	2191	91	78%
[NO$_3^-$]	70823	1771	81422	3387	-91%
[NO$_2^-$]	61447	1536	39254	1633	-6%
[PO$_4^{3-}$]	1191	30	<100	<4.16	>86%
[Cl$^-$]	1087	27	1028	43	-57%
[F$^-$]	776	19	214	8.9	54%
Al	7705	193	3765	157	19%
Cr	629	16	42	1.7	89%
Na	106000	2650	64850	2698	-2%
P	482	12	2.2	0.1	99%
S	5880	147	832	35	76%
Ca	21	0.5	18	0.75	-43%

Table 60. Addition of 40 mL of a 0.2 M Ba(NO₃)₂ Solution to 25 mL of an Envelope C Simulant. Barium to Sulfate Molar Ratio of 5.2:1 (Table 4.9 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	6350	159	2358	153	3%
[NO₃⁻]	178657	4466	81032	5267	-18%
[NO₂⁻]	49957	1249	18560	1206	3%
[PO₄³⁻]	2128	53	844	55	-3%
[Cl⁻]	1378	34	492	32	7%
[F⁻]	2863	72	1013	66	8%
Al	300	7.5	84	5.5	27%
Cr	134	3.4	38	2.5	26%
Na	157000	3925	58600	3809	3%
P	316	7.9	78	5.1	36%
S	2400	60	823	53	11%
Ca	330.0	8.3	46	2.99	64%

Table 61. Results of the TCLP on the Washed Precipitate from Table 60.

	Leachate Concentration mg/L
Ba	11124
Ca	20
Cd	<0.09
Cr	0.61
Pb	<0.18
S	1.62

Table 62. Addition of 80 mL of a 0.2 M Ba(NO₃)₂ Solution to 25 mL of an Envelope C Simulant. Barium to Sulfate Molar Ratio of 10.4:1 (Table 4.9 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
[SO₄²⁻]	6350	159	1321	139	13%
[NO₃⁻]	178657	4466	61789	6488	-45%
[NO₂⁻]	49957	1249	11217	1178	6%
[PO₄³⁻]	2128	53	520	55	-3%
[Cl⁻]	1378	34	323	34	2%
[F⁻]	2863	72	589	62	14%
Al	300	7.5	45	4.7	37%
Cr	134	3.4	17	1.8	47%
Na	157000	3925	36500	3833	2%
P	316	7.9	24	2.5	68%
S	2400	60	488	51	15%
Ca	330.0	8.3	25	2.63	68%

Table 63. Results of the TCLP on the Washed Precipitate from Table 62.

	Leachate Concentration mg/L
Ba	14229
Ca	47
Cd	<0.16
Cr	1.61
Pb	<0.31
S	3.10

Table 64. Addition of 136 mL of a 0.2 M Ba(NO₃)₂ Solution to 25 mL of an Envelope C Simulant. Barium to Sulfate Molar Ratio of 17.7:1 (Table 4.9 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	6350	159	229	37	77%
$[NO_3^-]$	178657	4466	51711	8325	-86%
$[NO_2^-]$	49957	1249	7382	1189	5%
$[PO_4^{3-}]$	2128	53	383	62	-16%
$[Cl^-]$	1378	34	243	39	-14%
$[F^-]$	2863	72	381	61	14%
Al	300	7.5	21	3.4	55%
Cr	134	3.4	7.1	1.1	66%
Na	157000	3925	24500	3945	0%
P	316	7.9	0.9	0.1	98%
S	2400	60	47	7.6	87%
Ca	330.0	8.3	17	2.74	67%

Table 65. Results of the TCLP on the Washed Precipitate from Table 64.

	Leachate Concentration mg/L
Ba	7290
Ca	10
Cd	<0.05
Cr	0.21
Pb	<0.10
S	0.60

Table 66. Addition of 4.75 mL of a 6.0 M Ca(NO₃)₂ Solution to 25 mL of an Envelope C Simulant followed by the Addition of 10.0 mL of 0.12 M Ba(NO₃)₂ Solution. Barium to Sulfate Molar Ratio of 0.8:1 (Table 4.9 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	6022	151	1195	48	68%
$[NO_3^-]$	171897	4297	189152	7519	-75%
$[NO_2^-]$	45357	1134	25957	1032	9%
$[PO_4^{3-}]$	1988	50	1851	74	-48%
$[Cl^-]$	1876	47	1472	59	-25%
$[F^-]$	2667	67	1027	41	39%
Al	295	7.4	79	3.1	57%
Cr	128	3.2	32	1.3	60%
Na	153000	3825	88850	3532	8%
P	325	8.1	0.9	0.04	100%
S	2330	58	54	2.1	96%
Ca	373	9.3	4430	176.09	-1788%

Table 67. Results of the TCLP on the Washed Precipitate from Table 66.

	Leachate Concentration mg/L
Ba	110
Ca	26
Cd	<0.02
Cr	0.3
Pb	<0.50
S	3.2

Table 68. Addition of 4.0 mL of a 15.4 M HNO₃ to 25 mL of an Envelope C Simulant followed by the Addition of 10.0 mL of 0.12 M Ba(NO₃)₂ Solution. Barium to Sulfate Molar Ratio of 0.8:1 (Table 4.9 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
$[SO_4^{2-}]$	6022	151	1111	43	71%
$[NO_3^-]$	171897	4297	210159	8196	-91%
$[NO_2^-]$	45357	1134	16137	629	44%
$[PO_4^{3-}]$	1988	50	374	15	71%
$[Cl^-]$	1876	47	1504	59	-25%
$[F^-]$	2667	67	1269	49	26%
Al	295	7.4	175	6.8	7%
Cr	128	3.2	76	3.0	7%
Na	153000	3825	95850	3738	2%
P	325	8.1	180	7.0	14%
S	2330	58	420	16	72%
Ca	373	9.3	217	8.46	9%

Table 69. Results of the TCLP on the Washed Precipitate from Table 68.

	Leachate Concentration mg/L
Ba	59
Ca	17
Cd	<0.02
Cr	0.1
Pb	<0.50
S	2.2

Table 70. Addition of 4.0 mL of a 15.4 M HNO₃ to 25 mL of an Envelope C Simulant (final pH of 5.9) followed by the Addition of 10.0 mL of 0.2 M Ba(NO₃)₂ Solution. Barium to Sulfate Molar Ratio of 1.3:1 (Table 4.10 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
Al	262	6.6	163	6.4	3%
Cr	139	3.5	78	3.0	12%
Na	152000	3800	98850	3855	-1%
P	324	8.1	167	6.5	20%
S	2445	61	65	2.5	96%

Table 71. Results of the TCLP on the Washed Precipitate from Table 70.

	Leachate Concentration mg/L
Ba	105
Ca	0
Cd	<0.05
Cr	0.25
Pb	0.15
S	2.3

Table 72. Addition of 7.1 mL of a 5.0 M Ca(NO$_3$)$_2$ Solution to 25 mL of an Envelope C Simulant followed by the Addition of 10.0 mL of 0.2 M Ba(NO$_3$)$_2$ Solution. Barium to Sulfate Molar Ratio of 1.3:1 (Table 4.10 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
Al	262	6.6	35	1.5	78%
Cr	139	3.5	25.6	1.1	69%
Na	152000	3800	98900	4164	-10%
P	324	8.1	1.0	0.04	99%
S	2445	61	31	1.3	98%

Table 73. Addition of 4.0 mL of a 15.4 M HNO$_3$ to 25 mL of an Envelope C Simulant (final pH of 5.9) followed by the Addition of 1.0 mL of 1.5 M Ba(NO$_2$)$_2$ Solution. Barium to Sulfate Molar Ratio of 0.8:1 (Table 4.10 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
Al	306	7.7	175	5.3	31%
Cr	135	3.4	101	3.0	10%
Na	147500	3688	128000	3840	-4%
P	370	9.3	177	5.3	43%
S	2300	58	329	10	83%

Table 74. Results of the TCLP on the Washed Precipitate from Table 73.

	Leachate Concentration mg/L
Ba	314
Ca	0
Cd	<0.02
Cr	<0.05
Pb	<0.50
S	2.9

Table 75. Addition of 4.0 mL of a 15.4 M HNO₃ to 25 mL of an Envelope C Simulant (final pH of 5.9) followed by the Addition of 1.75 mL of 1.5 M Ba(NO₂)₂ Solution. Barium to Sulfate Molar Ratio of 1.5:1 (Table 4.10 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
Al	306	7.7	169	5.2	32%
Cr	135	3.4	96	3.0	13%
Na	147500	3688	124000	3813	-3%
P	370	9.3	135	4.2	55%
S	2300	58	52	1.6	97%

Table 76. Results of the TCLP on the Washed Precipitate from Table 75.

	Leachate Concentration mg/L
Ba	812
Ca	0
Cd	<0.02
Cr	0.3
Pb	<0.50
S	2.6

Table 77. Addition of 4.5 mL of a 15.4 M HNO$_3$ to 25 mL of an Envelope C Simulant (final pH of 3.8) followed by the Addition of 1.75 mL of 1.5 M Ba(NO$_2$)$_2$ Solution. Barium to Sulfate Molar Ratio of 1.5:1 (Table 4.10 in Report)

	Envelope C Simulant mg/L	Envelope C Simulant mg	Final Solution mg/L	Final Solution mg	% Removed
Al	306	7.7	221	6.9	10%
Cr	135	3.4	108	3.4	0%
Na	147500	3688	131000	4094	-11%
P	370	9.3	220	6.9	26%
S	2300	58	19	0.6	99%

Table 78. Results of the TCLP on the Washed Precipitate from Table 77.

	Leachate Concentration mg/L
Ba	250
Ca	0
Cd	<0.02
Cr	0.1
Pb	<0.50
S	1.8

Table 79. Addition of 8.8 mL of a 15.4 M HNO$_3$ to 50 mL of an 241-AN-102 sample (final pH of 3.8) followed by the addition of 21 mL of 0.25 M Ba(NO$_3$)$_2$ Solution. Barium to Sulfate Molar Ratio of 1.5:1 (Table 4.11 in Report)

	Initial Composite Concentrations		Final Filtrate Concentrations		%
	Avg. mg/L	%RSD	Avg. mg/L	%RSD	Removed
[NO$_3^-$]	128941.0	4.33	183580.0	5.51	-127%
[NO$_2^-$]	41042.3	3.63	10940.0	11.0	57%
[PO$_4^{3-}$]	<3070		<3000		-56%
[SO$_4^{2-}$]	6554.9	3.40	<1500		63%
[C$_2$O$_4^{2-}$]	<3070		<3000		-56%
[Cl$^-$] (IC)	1617.6	5.78	850.0	26.9	16%
[F$^-$] (IC)	951.6	3.40	510.0	15.6	14%
[CHO$_2^-$]	5148.8	4.85	2920.0	4.75	9%
[OH$^-$]$_{free}$	17818.7	5.68	<1020		91%
[CO$_3^{2-}$]	31058.4	2.53	<3600		82%
[AlO$_2^-$]	7693.1	86.6	<3538		27%
[Cl$^-$] (ISE)	2883.8	6.98	2549.0	6.89	-41%
[F$^-$] (ISE)	<30.7		<30.0		-56%
TIC	5407.4	3.34	121	114	96%
TOC	31601.7	140	4816.0	6.48	76%
Al	7720	1.68	2110	3.30	56%
B	18.20	6.79	12.35	7.35	-8%
Ba	<0.614		2379.2	3.28	-618334%
Ca	254.0	3.23	130.1	4.03	18%
Cd	31.52	3.83	20.61	2.43	-4%
Co	3.081	27.7	5.440	4.14	-182%
Cr	112.6	3.41	38.1	4.15	46%
Cu	13.17	3.68	9.21	5.64	-12%
Fe	3.402	17.2	4.020	7.20	-89%
La	8.790	10.3	5.670	11.7	-3%
Li	<0.921		1.3400	18.6	-132%
Mg	1.319	2.75	<0.3000		64%
Mn	0.4920	14.4	0.6500	14.1	-111%
Mo	31.34	3.54	13.52	2.13	31%
Na	140001	3.40	83617	3.64	5%
Ni	211.3	2.86	134.9	4.36	-2%
P	981.6	2.60	235.4	4.35	62%
Pb	84.31	6.15	45.85	5.10	13%
Ru	16.47	11.4	20.29	4.62	-97%
Si	9.616	16.3	15.040	8.90	-150%
Sn	19.88	5.86	5.10	18.4	59%
Sr	140.1	6.56	15.7	3.69	82%
Tc	4.848	15.3	7.210	6.03	-137%
Ti	<0.614		2.1300	14.9	-454%
V	<1.259		3.830	10.2	-386%
Zn	5.314	5.78	<0.9000		73%
Zr	12.15	22.9	4.46	12.6	41%

Table 79. Continued

	Initial Composite Concentrations		Final Filtrate Concentrations		%
	Avg uCi/mL	%RSD	Avg uCi/mL	%RSD	Removed
Cs^{137}	198	7.59	110	1.11	11%
Pu^{238}	1.94E-03	3.98	8.68E-04	13.1	28%
$Pu^{239/240}$	1.56E-03	6.12	9.09E-04	13.5	7%
Cm^{244}	6.72E-01	78.1	4.56E-02	13.2	89%
Am^{241}	3.21E-02	2.92	1.34E-02	9.52	33%
Sr^{90}	2.06	4.96	0.14	4.66	89%
U^{235} ICP-MS	1.13E-07	2.44	8.02E-08	12.9	-13%
Np^{237} ICP-MS	4.60E-05	8.44	2.76E-05	2.28	4%
U^{238} ICP-MS	2.49E-06	5.32	1.56E-06	21.9	0%
Pu^{239} ICP-MS	1.18E-03	6.13	6.33E-04	7.96	14%
Tc^{99} ICP-MS	8.17E-02	2.80	6.01E-02	6.41	-17%

Table 80. Mass, Volume, and Density Measurements from the Acid Pre-Strike Barium Precipitation of 241-AN-102 Sample.

	Mass g	Volume mL	Density g/mL
Sample and Reagents Added			
Initial 241-AN-102 Sample	60.21	50	1.20
15.4 M HNO_3 Added	12.41	8.8	1.41
0.25 M $Ba(NO_3)_2$ added	21.84	21	1.04
Post Precipitation			
Wt % Insoluble solids	2.79%		
Final Filtrate	98.62	80	1.23
Settled Solids*		10	
Weight of dried solids	2.677		

*Solids settled in less than 1/2 hour.

Table 81. Composition of Combined Wash Solutions generated from washing the solids from the Acid Pre-Strike Treatment of the 241-AN-102 Sample.

	Acid Prestrike Wash Solutions	
	Avg. mg/L	%RSD
$[NO_3^-]$	52248	5.55
$[NO_2^-]$	3544	4.51
$[PO_4^{3-}]$	<381	
$[SO_4^{2-}]$	<190	
$[C_2O_4^{2-}]$	<381	
$[Cl^-]$ (IC)	258	4.13
$[F^-]$ (IC)	172	4.13
$[CHO_2^-]$	1220	2.88
$[OH^-]_{free}$	<1294	
$[CO_3^{2-}]$	<4568	
$[AlO_2^-]$	<4489	
$[Cl^-]$ (ISE)	413	14.2
$[F^-]$ (ISE)	<38.1	
TIC	70.6	61.3
TOC	2014	11.8
Al	426	3.48
B	3.02	15.1
Ba	546	2.80
Ca	58.3	5.89
Cd	7.02	2.08
Co	<1.98	
Cr	9.3	10.1
Cu	2.93	8.05
Fe	<1.18	
La	<4.19	
Li	<0.76	
Mg	<0.38	
Mn	<0.38	
Mo	2.81	7.46
Na	23539	3.10
Ni	41.1	1.09
P	42.5	6.09
Pb	17.8	9.99
Ru	<18.7	
Si	<6.09	
Sn	<5.71	
Sr	4.6	3.56
Tc	<2.66	
Ti	0.857	28.2
V	1.34	9.90
Zn	<1.14	
Zr	1.89	19.0
S (as SO4)	<41.9	

Table 81. Continued

	Acid Prestrike Wash Solutions	
	Avg uCi/mL	%RSD
Cs^{137}	30.92	3.46
Pu^{238}	4.56E-04	13.5
$Pu^{239/240}$	6.97E-04	30.3
Cm^{244}	1.69E-02	79.2
Am^{241}	4.68E-03	20.6
Sr^{90}	4.71E-02	6.47
U^{235} ICP-MS	1.40E-08	16.4
Np^{237} ICP-MS	8.57E-06	2.82
U^{238} ICP-MS	2.13E-07	4.73
Pu^{239} ICP-MS	2.01E-04	17.4
Tc^{99} ICP-MS	1.42E-02	5.32

Table 82. Addition of 150 mL of 0.25 M Ba(NO₃)₂ Solution to 50 mL of an 241-AN-102 sample. Barium to Sulfate Molar Ratio of 1.5:1 (Table 4.11 in Report)

	Initial Composite Concentrations		Final Filtrate Concentrations		% Removed
	Avg. mg/L	%RSD	Avg. mg/L	%RSD	
$[NO_3^-]$	128941	4.33	50830	1.99	-59%
$[NO_2^-]$	41042	3.63	10944	0.69	-8%
$[PO_4^{3-}]$	<3070		<292.0		62%
$[SO_4^{2-}]$	6554.9	3.40	<146.0		91%
$[C_2O_4^{2-}]$	<3070		<292.0		62%
$[Cl^-]$ (IC)	1617.6	5.78	408.3	4.41	-2%
$[F^-]$ (IC)	951.6	3.40	223.9	8.06	5%
$[CHO_2^-]$	5148.8	4.85	1254.5	1.91	2%
$[OH^-]_{free}$	17818.7	5.68	1900.1	17.1	57%
$[CO_3^{2-}]$	31058.4	2.53	<3504		54%
$[AlO_2^-]$	7693.1	86.6	9873.8	13.7	-419%
$[Cl^-]$ (ISE)	2883.8	6.98	1953.4	9.58	-174%
$[F^-]$ (ISE)	<30.7000		<29.2000		
TIC	5407.4	3.34	11841.6	94.9	-785%
TOC	31601.7	140	22464.1	83.2	-187%
Al	7720	1.68	1793	0.55	6%
B	18.20	6.79	4.15	8.95	8%
Ba	<0.614	0.00	2112.8663	0.64	-1390125%
Ca	254.0	3.23	28.7	2.00	54%
Cd	31.52	3.83	7.17	4.18	8%
Co	3.081	27.7	<1.8151		-138%
Cr	112.6	3.41	<2.1876		92%
Cu	13.17	3.68	3.39	12.2	-4%
Fe	3.402	17.2	<1.0291		-22%

Table 82. Continued

	Initial Composite Concentrations		Final Filtrate Concentrations		% Removed
	Avg. mg/L	%RSD	Avg. mg/L	%RSD	
La	8.790	10.4	<3.4392		-58%
Li	<0.921		<0.5840		-156%
Mg	1.319	2.75	0.435	34.5	-33%
Mn	0.4920	14.4	<0.2920		-140%
Mo	31.34	3.54	5.92	1.02	24%
Na	140001	3.40	32080	0.26	7%
Ni	211.3	2.86	50.7	1.94	3%
P	981.6	2.60	16.3	25.5	93%
Pb	84.31	6.15	17.21	15.1	18%
Ru	16.47	11.4	<14.3080		-251%
Si	9.616	16.3	<4.6720		-96%
Sn	19.88	5.86	4.53	6.18	8%
Sr	140.1	6.56	1.4	3.00	96%
Tc	4.848	15.3	2.798	12.16	-133%
Ti	<0.614		<0.6719		-342%
V	<1.259		<1.0212		-228%
Zn	5.314	5.78	1.649	19.4	-25%
Zr	12.15	22.9	<1.2248		59%
Cs^{137}	198	7.59	44.1	1.19	10%
Pu^{238}	1.94E-03	3.98	4.49E-04	13.5	6%
$Pu^{239/240}$	1.56E-03	6.12	1.22E-03	47.3	-217%
Cm^{244}	6.72E-01	78.1	1.54E-02	138	91%
Am^{241}	3.21E-02	2.92	8.33E-04	16.5	90%
Sr^{90}	2.0628	4.96	4.66E-03		99%
Tc^{99} ICP-MS	8.17E-02	2.80	2.19E-02	5.36	-8%

Table 83. Mass, Volume, and Density Measurements from the Barium Precipitation of 241-AN-102 Sample (see Table 82).

	Mass	Vol	density
Sample and Reagents Added			
Initial 241-AN-102 Sample	61.33	50	1.23
0.25 M Ba(NO3)2 Added	158.08	152	1.04
Post Precip			
Wt% Insoluble solids	3.25%		
Final Filtrate	198.56	200	0.99
Settled Solids		15	
Weight of dried solids	6.67		

*Solids settled in less than 1/2 hour.

Table 84. Composition of Combined Wash Solutions generated from washing the solids from the Barium Nitrate Addition to the 241-AN-102 Sample.

	Barium Addition Wash Solutions	
	Avg. mg/L	%RSD
$[NO_3^-]$	11328	1.30
$[NO_2^-]$	1848	1.81
$[PO_4^{3-}]$	<315	
$[SO_4^{2-}]$	<158	
$[C_2O_4^{2-}]$	<315	
$[Cl^-]$ (IC)	73.4	24.2
$[F^-]$ (IC)	63.0	1.10
$[CHO_2^-]$	241	6.48
$[OH^-]_{free}$	<1124	
$[CO_3^{2-}]$	<3780	
$[AlO_2^-]$	<3714	
$[Cl^-]$ (ISE)	126	43.7
$[F^-]$ (ISE)	<31.5	
TIC	223	8.48
TOC	284	17.0
Al	344	1.99
B	<1.58	
Ba	155	47.3
Ca	19.9	15.5
Cd	2.14	3.66
Co	<1.58	
Cr	<2.21	
Cu	1.22	14.3
Fe	<0.95	
La	<3.47	
Li	<0.63	
Mg	<0.32	
Mn	<0.32	
Mo	2.19	23.4
Na	6354	1.60
Ni	9.9	3.61
P	<8.19	
Pb	11.62	41.3
Ru	<15.4	
Si	<5.04	
Sn	<4.73	
Sr	<0.35	
Tc	<2.21	
Ti	<0.65	5.10
V	<1.08	18.9
Zn	<0.95	
Zr	1.48	13.6
S (as SO4)	<34.7	

Table 84. Continued

	Barium Addition Wash Solutions	
	Avg uCi/mL	%RSD
Cs^{137}	8.37	1.03
Pu^{238}	3.06E-04	41.1
$Pu^{239/240}$	8.73E-04	43.0
Cm^{244}	3.13E-03	102
Am^{241}	<1.33E-03	
Sr^{90}	9.26E-04	13.4
Tc^{99} ICP-MS	6.40E-03	5.23

Appendix 3

ENVELOPE A

Tank AN105 Supernate Composition

Component	Molecular weight	Concentration	Units	Concentration	Units
Acetate	59.04462	2070	mg/Liter	3.51E-02	M
Aluminum	26.98154	39700	mg/Liter	1.47E+00	M
Ammonium	18.03846	120	mg/Liter	6.65E-03	M
Boron	10.81	51	mg/Liter	4.72E-03	M
Calcium	40.08	40	mg/Liter	9.98E-04	M
Carbonate	60.0092	12540	mg/Liter	2.09E-01	M
Cesium	132.9054	16	mg/Liter	1.22E-04	M
Chloride	35.453	9090	mg/Liter	2.56E-01	M
Chromium	51.996	1350	mg/Liter	2.60E-02	M
Fluoride	18.9984	190	mg/Liter	1.00E-02	M
Formate	45.01774	2880	mg/Liter	6.40E-02	M
Glycolate	75.04206	1150	mg/Liter	1.53E-02	M
Hydroxide	17.00734	58100	mg/Liter	3.42E+00	M
Magnesium	24.305	5	mg/Liter	2.22E-04	M
Molybdenum	95.94	82	mg/Liter	8.55E-04	M
Nitrate	62.0049	165000	mg/Liter	2.66E+00	M
Nitrite	46.0055	111000	mg/Liter	2.41E+00	M
Oxalate	88.0196	610	mg/Liter	6.93E-03	M
Phosphate	94.97136	570	mg/Liter	6.00E-03	M
Potassium	39.0983	7500	mg/Liter	1.92E-01	M
Selenium	78.96	1	mg/Liter	1.25E-05	M
Silicon	28.0855	211	mg/Liter	7.51E-03	M
Sodium	22.9898	233000	mg/Liter	1.01E+01	M
Sulfate	96.0576	771	mg/Liter	8.03E-03	M
TIC	12.011	2510	mg/Liter	2.09E-01	M
TOC		3590	mg/Liter	3.59	g/L
Zinc	65.38	10	mg/Liter	1.54E-04	M
Density (average)		1.4			

ENVELOPE B

Tank AZ101 Supernate Composition

Component	Molecular weight	Concentration	Units	Concentration	Units
Aluminum	26.98154	10667.7	mg/Liter	3.95E-01	Molar
Ammonia	17.03052	312.8	mg/Liter	1.84E-02	Molar
Carbonate	60.0092	23075.8	mg/Liter	3.85E-01	Molar
Cesium	132.9054	37.3	mg/Liter	2.81E-04	Molar
Chloride	35.453	199.5	mg/Liter	5.63E-03	Molar
Chromium	51.996	729.9	mg/Liter	1.40E-02	Molar
Fluoride	18.998	1813.2	mg/Liter	9.54E-02	Molar
Hydroxide	17.00734	9029.6	mg/Liter	5.31E-01	Molar
Nitrate	62.0049	75631.6	mg/Liter	1.22E+00	Molar
Nitrite	46.0055	65063.0	mg/Liter	1.41E+00	Molar
Phosphate	94.97136	1502.7	mg/Liter	1.58E-02	Molar
Potassium	39.0983	4623.8	mg/Liter	1.18E-01	Molar
Sodium	22.9898	108988.8	mg/Liter	4.74E+00	Molar
Sulfate	96.0576	17669.4	mg/Liter	1.84E-01	Molar
TIC	12.011	4618.7	mg/Liter	3.85E-01	Molar
Zirconium	91.22	3.1	mg/Liter	3.37E-05	Molar

ENVELOPE C

Tank AN-107 Supernate Composition - Recipe For AN-107 Supernate Simulant formulated by R. Eibling

Note: Barium, lead, and chromium compounds were omitted in the current work.

Component	Molecular Weight	Concentration	Units	Concentration	Units
Acetate	59.04462	1100	mg/Liter	1.86E-02	M
Aluminum	26.98154	386	mg/Liter	1.43E-02	M
Ammonium	18.03846	22	mg/Liter	1.22E-03	M
Barium	137.33	7	mg/Liter	5.42E-05	M
Boron	10.81	35	mg/Liter	3.24E-03	M
Bromide	79.904	1150	mg/Liter	1.44E-02	M
Calcium	40.08	591	mg/Liter	1.47E-02	M
Carbonate	60.0092	83936	mg/Liter	1.40E+00	M
Cerium	140.12	53	mg/Liter	3.77E-04	M
Chloride	35.453	1830	mg/Liter	5.16E-02	M
Chromium	51.996	176	mg/Liter	3.38E-03	M
Copper	63.546	30	mg/Liter	4.74E-04	M
EDTA	288.20824	5620	mg/Liter	1.95E-02	M
Fluoride	18.9984	133	mg/Liter	7.00E-03	M
Formate	45.01774	10400	mg/Liter	2.31E-01	M
Glycolate	75.04206	18600	mg/Liter	2.48E-01	M
Hydroxide	17.00734	340	mg/Liter	2.00E-02	M
Iron	55.847	1690	mg/Liter	3.03E-02	M
Lanthanum	138.9055	46	mg/Liter	3.28E-04	M
Lead	207.2	388	mg/Liter	1.87E-03	M
Magnesium	24.305	25	mg/Liter	1.03E-03	M
Manganese	54.938	563	mg/Liter	1.02E-02	M
Molybdenum	95.94	36	mg/Liter	3.73E-04	M
Neodymium	144.24	96	mg/Liter	6.65E-04	M
HEDTA	275.23618	2140	mg/Liter	7.78E-03	M
Nickel	58.69	530	mg/Liter	9.03E-03	M
Nitrate	62.0049	230000	mg/Liter	3.71E+00	M
Nitrite	46.0055	61000	mg/Liter	1.33E+00	M
Oxalate	88.0196	826	mg/Liter	9.38E-03	M
Phosphate	94.97136	1110	mg/Liter	1.17E-02	M
Potassium	39.0983	1810	mg/Liter	4.63E-02	M
Selenium	78.96	1	mg/Liter	6.33E-06	M
Silver	107.8682	14	mg/Liter	1.33E-04	M
Sodium	22.9898	195000	mg/Liter	8.48E+00	M
Sulfate	96.0576	8250	mg/Liter	8.59E-02	M
TIC	12.011	16800	mg/Liter	1.40E+00	M
TOC		40400	mg/Liter	40.40	g/L
Zinc	65.38	45	mg/Liter	6.93E-04	M
Zirconium	91.22	70	mg/Liter	7.67E-04	M
Additional Organics(based upon PNNL Report on FY1997 Results)					
Nitrilotriacetic Acid	188.11618	561	mg/Liter	2.98E-03	M
Citric Acid	189.09618	8495	mg/Liter	4.49E-02	M
Iminodiacetic Acid	131.08412	5947	mg/Liter	4.54E-02	M
Source	Agreement on Gluconate from Bill Wilmarth based upon Fe titration Test				
Sodium Gluconate	218.14	3927	mg/Liter	1.80E-02	M
Density (average)		1.4			

Appendix 4

Pictures from:

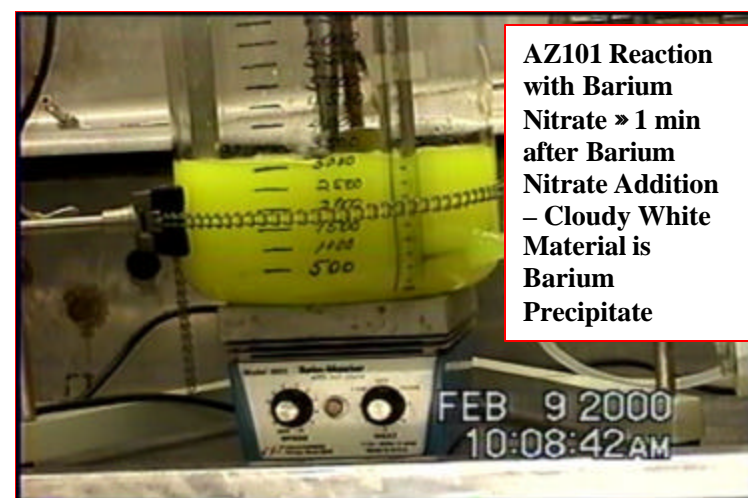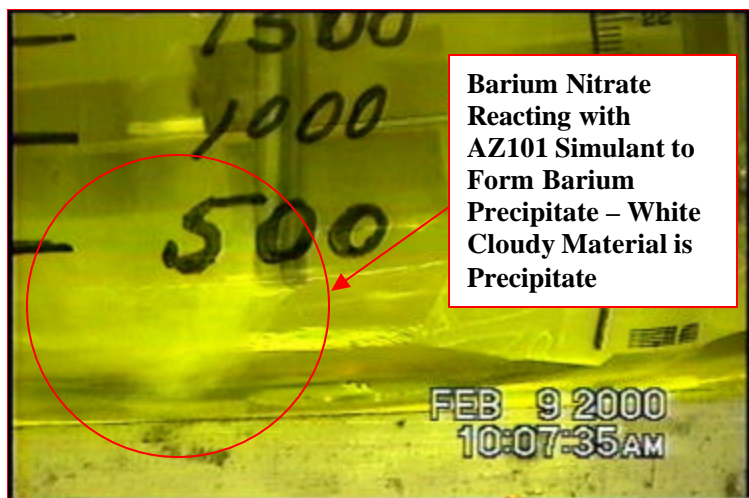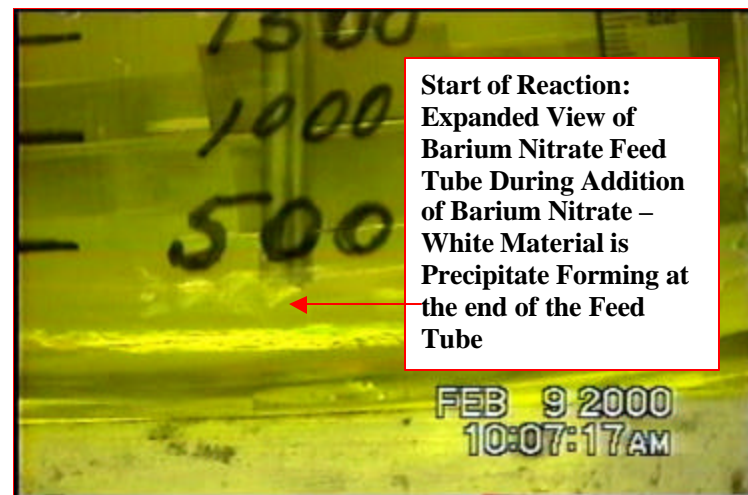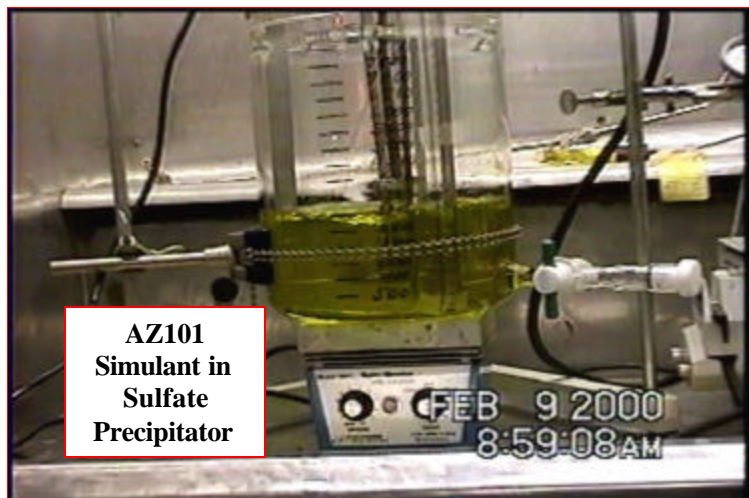**Section 6.0: Bench Scale Precipitation and Evaporation of an Envelope B Simulant**

Section 8.0: Feed Stream Evaporation and Waste Glass Formulation for a Sulfate Pretreated Envelope C AN-102 Sample
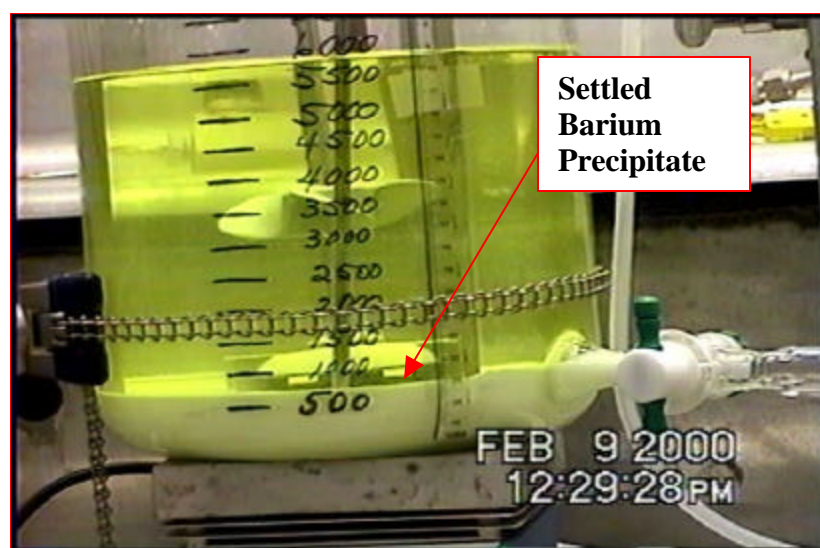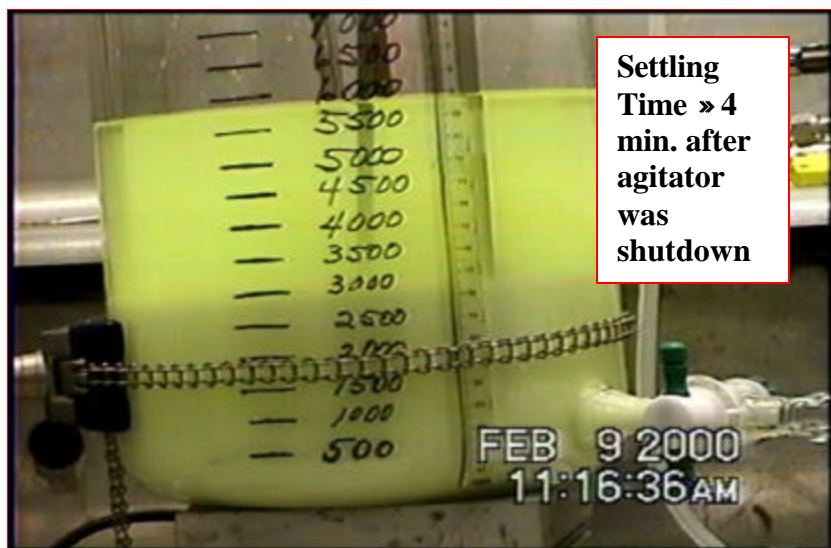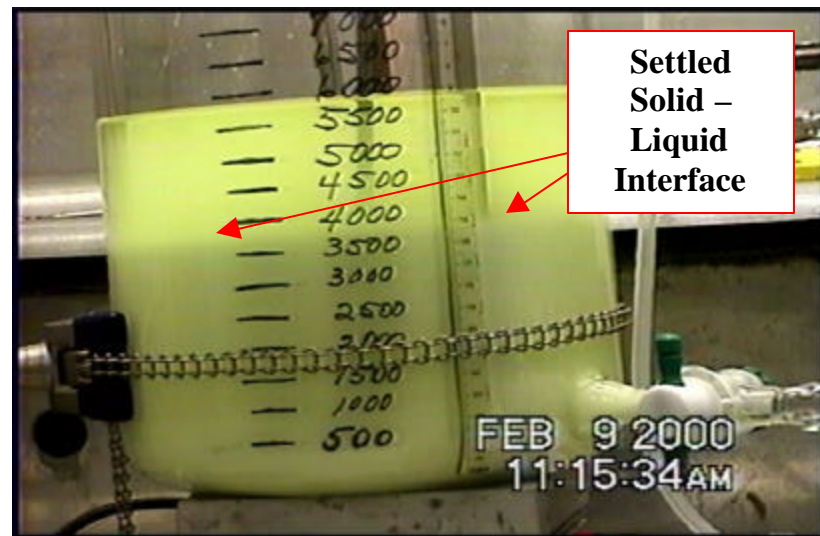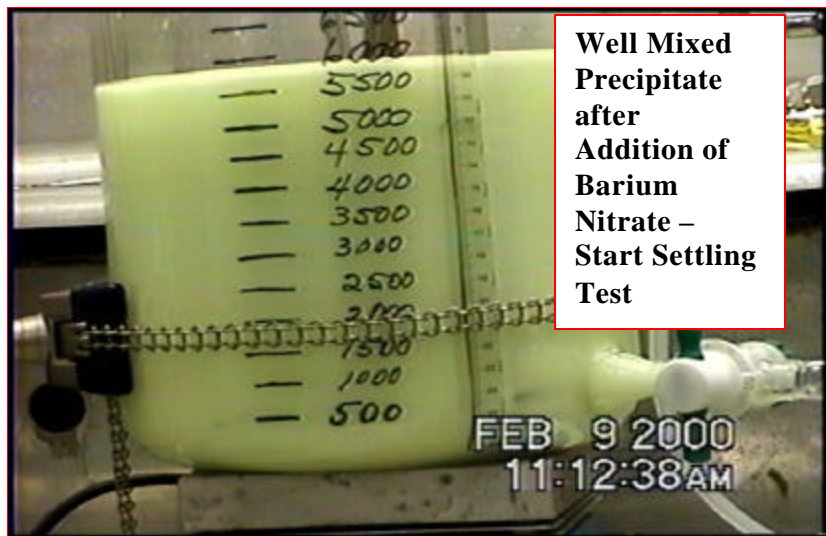
From Section 6.0,

AZ-101 Simulant Sulfate Precipitation by Addition of Barium Nitrate Solution

The barium nitrate solution was added to the AZ101 simulant in a well-agitated vessel. A peristaltic pump was use to add the barium nitrate solution at a rate of 10 ml/min. The 0.27 M barium nitrate solution was added to achieve a molar ratio of 1.3 moles of Ba per mole SO_4 (0.789 g $Ba(NO_3)_2$ solution / g AZ101 simulant) in the combined mixture. The reaction vessel and pictures of the initial reaction of barium nitrate with the AZ101 simulant are shown below. The reaction is immediate.
A settling test was conducted after the barium nitrate addition was completed. The settling rate pictures are shown below. The barium precipitate settles rapidly and can be characterized as a fast settling heterogeneous slurry. The barium precipitate settled to approximately 20 volume % at a settling rate of approximately 2 cm/min

AZ101 Simulant in Sulfate Precipitator

Start of Reaction: Expanded View of Barium Nitrate Feed Tube During Addition of Barium Nitrate – White Material is Precipitate Forming at the end of the Feed Tube

Barium Nitrate Reacting with AZ101 Simulant to Form Barium Precipitate – White Cloudy Material is Precipitate

AZ101 Reaction with Barium Nitrate ➤ 1 min after Barium Nitrate Addition – Cloudy White Material is Barium Precipitate

Precipitation of Sulfate from AZ101 – Initial Reaction of Barium Nitrate with AZ101 Simulant

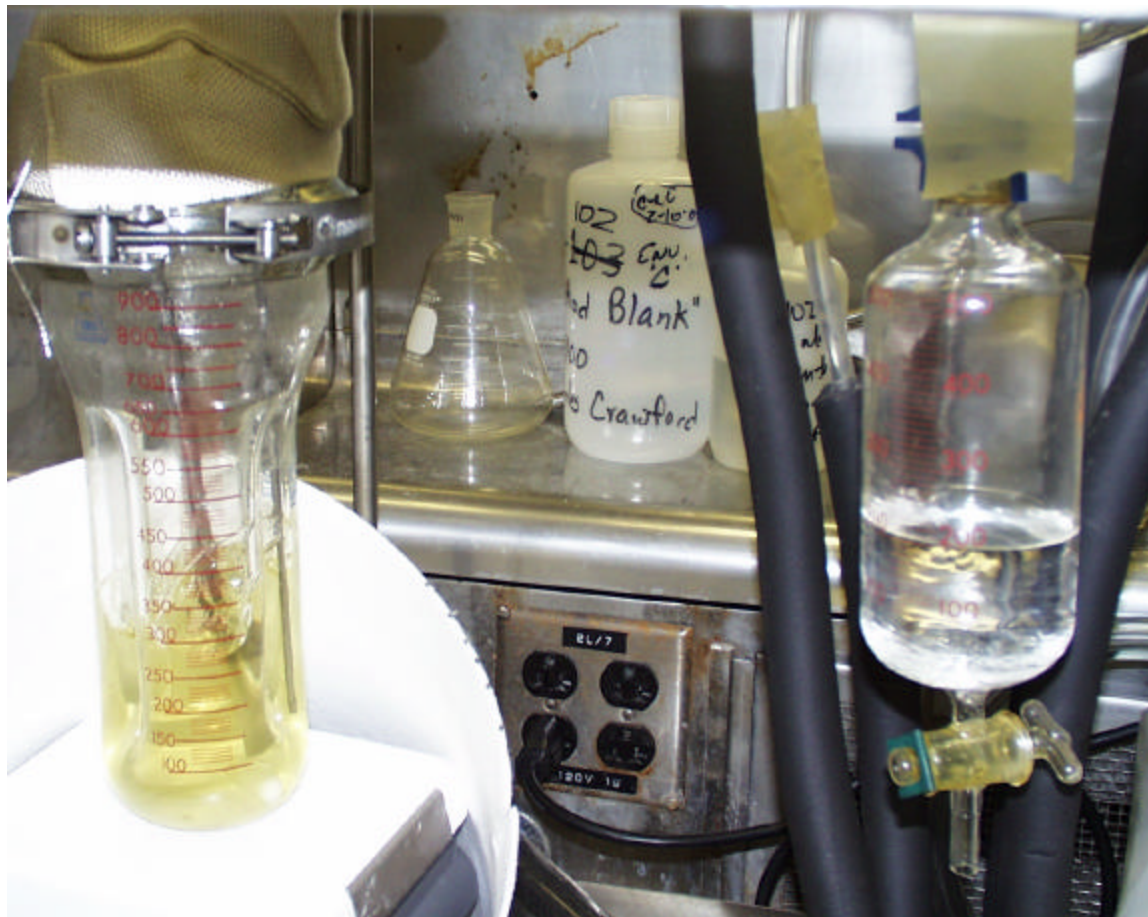**Barium Sulfate Slurry Settling Rate Test**

From Section 8.0,

Env. C Decontaminated Active Sample Evaporation

Photographs of the Decontaminated AN-102 Evaporation Tests

After initial evaporation of ~ 100 mL of condensate from initial charge of ~ 550 mL of evaporator feed; 2/22/00 @ 08:30

After further evaporation of ~ 200 mL of condensate from initial charge of ~ 550 mL of evaporator feed; 2/22/00 @ 11:00

**After further evaporation of ~ 300 mL of condensate from initial charge of
~ 550 mL of evaporator feed; 2/22/00 @ 12:30**

After charging pot, evaporation of ~ 190 mL of condensate. The condensate was collected and added to the polybottle located on back shelf in middle of picture; 2/22/00 @ 19:00

After final stage of evaporation; 2/23/00 @ 16:45

Final experiment showing ~ 220 mL of concentrate and ~ 800 mL of condensate (combined from 1-Liter polybottle and glass condensate collector); 2/23/00 @ 16:45

Final experiment, different angle; 2/23/00 @ 16:45