

## **Preliminary Evaluation of Am/Cm Melter Feed Preparation Process Upset Recovery Flowsheets**

by

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PRELIMINARY EVALUATION OF AM/CM MELTER FEED  
PREPARATION PROCESS UPSET RECOVERY FLOWSHEETS

The attached document summarizes the results from the development of flowsheets to recover from credible processing errors specified in TTR 99-MNSS/SE-006. The proposed flowsheets were developed in laboratory scale equipment and will be utilized with minor modifications for full scale demonstrations in the Am/Cm Pilot Facility. Please refer any questions you may have regarding the contents of this document to M. E. Stone (Ext. 7-7751)

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**PRELIMINARY EVALUATION OF AM/CM MELTER  
FEED PREPARATION PROCESS UPSET RECOVERY  
FLOWSHEETS (U)**

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# PRELIMINARY EVALUATION OF AM/CM MELTER FEED PREPARATION PROCESS UPSET RECOVERY FLOWSHEETS (U)

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## SUMMARY

Proposed flowsheets were developed to recover from credible processing errors as defined by NMSS Technical Task Request 99-NMSS/SE-006. Specifically,

- Develop a recovery method for processing a diluted feed.
- Develop a recovery method from the addition of 50 wt% nitric acid in lieu of 8 wt% oxalic acid
- Develop a recovery method from the addition of 0.1M oxalic acid in lieu of 8 wt% oxalic acid

Scoping, lab-scale (1/14) tests were conducted to verify the proposed flowsheets prior to full-scale demonstrations. These tests were conducted under the Technical Task Plan, WSRC-RP-99-0610.

## BACKGROUND

The americium and curium currently stored in F-canyon will be vitrified using a batch process that performs an oxalate precipitation process to de-nitrate the melter feed. This process has been demonstrated and tested on lab-scale (1/70, 1/7, and 2/7 scale) as well as full scale processes. A non-radioactive surrogate feed was used to perform the tests. The surrogate feed is a one molar nitric acid solution containing 100 grams per liter of solids (oxide basis) with a lanthanide content of 89.9 grams per liter (oxide basis). A constant volume of feed is added to the precipitator through the use of an overflow in the Batch Tank. Eight weight percent oxalic acid is metered into the precipitation vessel, which is held at 30 degrees Celsius, to precipitate the lanthanides from the solution. The solids are allowed to settle and the spent precipitant solution decanted from the vessel leaving approximately 2500 milliliters of solution and solids in the vessel. 0.1M oxalic acid is then added to wash the solids. After settling the solids and decanting the spent wash, the resulting de-nitrated slurry is transferred by gravity to the melter.

The proposed flowsheets for recovering from the upsets conditions are documented in SRT-AMC-99-0169. Acceptability of the proposed flowsheets will be determined by the same requirements used during the Demonstration Runs (SRT-AMC-98-0300): no spillage or overflow during operation, recovery of lanthanides > 95%, holdup in the precipitator < 2%, and no spillage or overflow during transfer of oxalate to the melter. During the lab-scale runs, acceptability will be determined by engineering judgement that the proposed flowsheet would meet the above requirements when full scale tests are conducted.

## EVALUATION

Tests were conducted using 0.5 liters of surrogate feed for each precipitation batch. Surrogate SURR-1449, made up per SRT-AMC-98-0088, was used for all runs to allow direct comparison of results. Table 1 shows the common parameters used during all runs.

Table 1. Common Parameters for All Lab-Scale Tests

	Lab - Scale	Full - Scale	Units
Surrogate Feed Sample Number	SURR-1449	-	
Vessel Size	4	25	liters
Agitator Impeller Diameter	2	3	inches
Number of Impellers	1	2	
Agitator Speed	200	450	RPM
Decant Tube Position	181	2500	milliliters
Surrogate Feed per Batch	500	6,910	milliliters
Ratio of wash solution:surrogate	1:1	1:1	
Precipitator Temperature	30	30	°C
8 wt% Oxalic Acid Temperature	30	30	°C
Digestion Time	10	10	Minutes
Settling Time	15	30	Minutes
Mixing Time for Wash	5	10	Minutes
Decant Rate	300	-	ml/min

### Equipment Setup

The equipment setup is shown in Attachment I. A four-liter, water-jacketed, glass precipitator with a conical bottom was used to perform the precipitation tests. A water-jacketed vessel was also used for the 8 wt% oxalic acid tank.

### Baseline Runs (LS-502 and LS-508)

Two runs using the baseline process were conducted to provide a comparison point to evaluate the test runs against. The results from the baseline tests were scaled up for comparison to full scale runs in Coupled Precipitator One. The yield for both the lab-scale and full scale runs was >99.7%. The settled solids volume of 141 ml for the baseline run scales to 1949 ml which is in good agreement with the 1900 ml measured for the full scale process. Based on these results, it is assumed that the full scale process parameters can be scaled directly from the lab-scale runs. Process parameters used for the baseline runs and the process results are shown in Table 2.

### Dilute Feed Runs

Dilute feed runs were performed with surrogate feed of 50, 33, and 25 grams per liter (oxide basis). The flowsheet tested utilized a "multiple batch" precipitation process that provided the equivalent of one baseline precipitation batch to the melter for vitrification. The first batch was precipitated, settled, and decanted. The second batch of feed was then added to the vessel on top of the solids from the first batch. The second batch was then precipitated, settled, and decanted. After all batches were precipitated and decanted,

the solids were washed and then transferred to a beaker for solids volume measurement and sampling.

The oxalic acid addition amount was adjusted for each run to maintain 0.275M excess oxalic acid concentration at the end of each batch. The oxalic acid rate of addition was slowed to maintain a precipitation time of 35 minutes, except for LS-507. During LS-507, the oxalic acid addition rate was maintained at the baseline rate and the addition time was reduced. Two runs were conducted with feed diluted with process water (LS-503 and LS-505) and three runs (LS-504, LS-506, and LS-507) were conducted with feed diluted with 1M nitric acid.

The precipitation yield was acceptable for all runs and denitration was comparable to the baseline flowsheet. Settled solids volume was impacted by the change in process method. Runs diluted with process water showed an upward trend in settled solids volume, while runs diluted with nitric acid showed a downward trend, as shown in Table 2 and Figure 1. Based on the results, it is recommended that the process feed be maintained at 1M nitric acid.

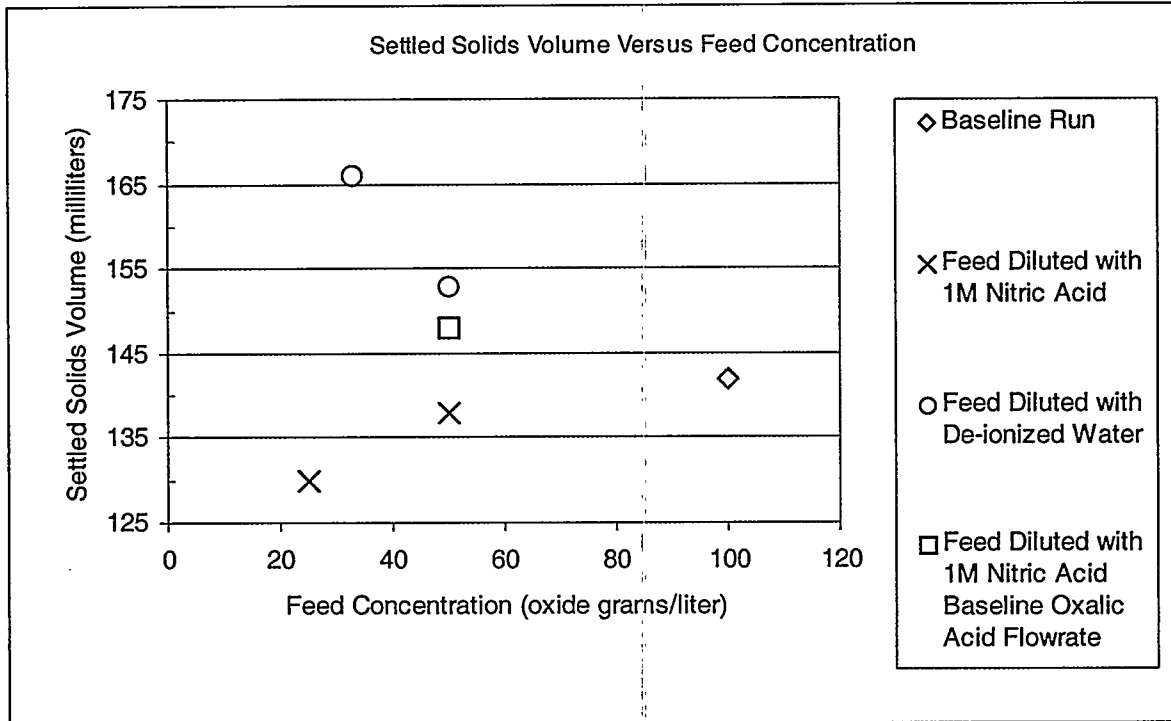
Processing with the baseline oxalic acid addition rate increased the settled solids volume, but did not impact solids volume as much as nitric acid molarity.

Table 2. Process Parameters and Results: Non-Baseline Tests (Dilute Feed)

Process Parameters	Baseline LS-502 LS-508	LS-503	LS-504	LS-505	LS-506	LS-507	Units
Feed Oxide Conc.	100	50	50	33	25	50	g/L
Feed Nitric Molarity	1.0	0.5	1.0	0.33	1.0	1.0	Molar
Number of Batches	1	2	2	3	4	2	
8 wt% Oxalic Acid Amount per Batch	870	546	546	440	386	546	ml
Oxalic Acid Rate	24.9	15.6	15.6	12.6	11.0	24.9	ml/min
Addition Time	35	35	35	35	35	22	minutes
Dilution Chemical	-	DI Water	1M HNO3	DI Water	1M HNO3	1M HNO3	
<b>Test Results*</b>							
Entrained Solids	0.0190	0.0196	0.0525	0.0403	0.0885	0.0564	grams
Precipitation Yield	>99.7	99.7	99.6	99.6	99.4	99.6	%
Solids Volume	141	153	138	166	130	148	ml
Nitrate in Wash	13,500	11,600	12,600	8,690	12,500	14,100	ppm
Particle Size (mean)	123	102	123	94	113	118	microns
Particle Size (std dev)	45.5	42	49	42	52	43	
% <15.56 micron	0.14	0.57	0.13	1.24	0.35	0.16	%

\*Results for Baseline Run are the average of results for LS-502 and LS-508

Figure 1. Settled Solids Volumes for Dilute Feed Runs



**Recovery from Addition of 50 wt% HNO<sub>3</sub> in Lieu of 8 wt% Oxalic Acid**

The inadvertent addition of 50% nitric acid (~10M) would result in a diluted solution that requires adjustment to 1M nitric acid prior to precipitation. Adjustment by dilution with water would exceed the volume of any vessel in the MPPF preliminary design. A literature review was conducted to determine if a metal hydroxide could be used to neutralize the nitric acid prior to precipitation. The transition elements interfere with the precipitation process by complexing with oxalate at high concentrations, resulting in very low yields for the actinides. The alkali metals would likely be precipitated by the oxalate at the concentrations required, resulting in incomplete separation and a melter feed containing very high impurity levels.

The recovery method tested utilized the addition of solid lanthanum oxide and dilution water to create a solution that is 1M nitric acid and has a lanthanide content of 89.9 grams per liter (oxide basis), matching the conditions of “normal” precipitator feed. The solution was then processed using the baseline precipitation process.

Eighty milliliters of SURR-1449, 139 milliliters of 50% nitric acid, and 386 milliliters of dilution water were added to an Erlenmeyer flask on a stir plate. 47.1 grams of lanthanum oxide were slowly added to the vessel. Some of the lanthanum oxide solids settled to the bottom, but were incorporated into the solution within 10 minutes. The resulting 600 ml of solution was sampled for nitric acid molarity and lanthanide content.

The results indicated the solution was 1.11M nitric acid with a lanthanide content of 99 grams per liter (oxide basis). 500 ml of this solution was precipitated using the baseline precipitation flowsheet.

The precipitation yield based on soluble losses was >98.6%, but this value was limited by the detection limits of the analytical method. Settled solids volume was lower than the baseline run while the amount of nitrate in the melter feed was not significantly increased (~10% higher), as shown in Table 3.

Table 3. Process Parameters and Test Results: 50% HNO<sub>3</sub> Recovery

Process Parameters	LS-509	Units
Surrogate Feed Volume	80	milliliters
50% Nitric Acid Addition	139	milliliters
Dilution Water Addition	386	milliliters
Lanthanum Oxide	47.1	grams
8 wt% Oxalic Acid Amount	870	ml
Oxalic Acid Rate	24.9	ml/min
Addition Time	35	minutes
Process Results		
Surrogate Feed Molarity	1.107	Molar
Surrogate Feed Concentration	99	Grams/liter lanthanide oxide
Entrained Solids	0.0789	grams
Precipitation Yield	98.6	%
Solids Volume	138	ml
Nitrate in Wash	14,800	ppm
Particle Size (mean)	154	microns
Particle Size (std dev)	55	
% <15.56 micron	0.00	%

#### Recovery from Addition of 0.1M Oxalic Acid in Lieu of 8 wt% Oxalic Acid

The addition of dilute oxalic acid (0.1M) in place of 8 wt% oxalic acid would result in partial precipitation of the lanthanides. The resulting solution would contain a large amount of solids and would be difficult to recycle. Addition of solid oxalic acid to the precipitator vessel to precipitate the lanthanides and provide 0.275M excess oxalic acid was tested. The oxalate solids were added prior to decanting the spent precipitant. The precipitated solids were then allowed to settle and the excess solution decanted. After washing, the resulting slurry was transferred to a beaker.

Three process tests (LS-510, LS-511, and LS-512) were conducted to test the proposed flowsheet for recovery from an inadvertent addition of 0.1M oxalic acid in place of 8 wt% oxalic acid. All three tests involved adding solid oxalic acid to the precipitator to precipitate the lanthanides and provide 0.275M excess oxalic acid. During LS-511 and LS-512, the nitric acid concentration was adjusted to 1.0M prior to addition of the oxalic acid crystals, no adjustment was made during LS-510. The addition rate of oxalic acid solids was <1 minute for LS-510, 23 minutes for LS-511, and 44 minutes for LS-512.

The 0.1M oxalic acid was metered into the vessel over 35 minutes at 30 degrees Celcius. Initially, the addition caused a small cloud to form around the feed tube, but the solids were quickly redissolved as they mixed with the solution in the vessel. After approximately 20 minutes, the solution in the vessel began to become murky as the solids no longer redissolved. At the end of the addition, the suspended solids were present in large amounts and were evenly distributed throughout the solution during the digestion period. During the baseline and other runs, the top 2-3 inches of solution remained fairly free of solids during this period.

During LS-510, the rapid introduction of oxalic acid caused very large clumps to drop to the bottom of the precipitator. These clumps broke up over 2-3 minutes during the digestion period and resulted in suspended solids evenly distributed throughout the vessel. The observed settling time was greatly increased from the baseline run, although the 15 minute period allowed by the baseline run plan was adequate, and the settled solids volume was nearly doubled from the baseline run as shown in Table 4. The settled solids were much higher than the decant tube and the run was aborted. Particle size analysis indicated a much smaller and widely distributed particle size, with the presence of great numbers of fines.

Two factors contributed to the failure of LS-510: the rapid addition of the oxalic acid and the low feed nitric acid molarity (~0.3M) during the precipitation process. During LS-511 and LS-512, the solution was adjusted to 1.0 molar nitric acid prior to addition of the solid oxalic acid. The solid oxalic acid feed rate was adjusted to 4 grams of crystals per minute (addition time: 22 minutes) for LS-511. This run was also aborted due to high settled solids volume (161 ml). The oxalic acid feed rate for LS-512 was 2 grams per minute (addition time: 44 minutes). The settled solids volume was 152 ml, which scales to 2,100 ml during a full-scale run. The dip tube on CP-1 is set at 2,500 ml which should allow sufficient free solution to perform a run using the method tested during LS-512. Two washes were required to denitrate the feed due to the additional nitric acid addition.

Yield for LS-512 was not adversely impacted by the adjustment to 1M nitric acid, as the yield of 99.4% matched the baseline run. The amount of nitrate in the melter feed was not measured accurately due to the decant dip leg slipping below the normal setting during the process.

Table 4. Process Parameters and Results: 0.1M Oxalic Acid Recovery

Process Parameters	LS-510	LS-511	LS-512	Units
0.1M Oxalic Acid Amount	870	870	870	MI
Oxalic Acid Rate	24.9	24.9	24.9	ml/min
Addition Time	35	35	35	Minutes
50% Nitric Acid Addition	-	100	100	MI
Dilution Water Addition	-	30	30	MI
Solid Oxalic Acid Amount	86.5	86.5	86.5	Grams
Addition Rate	86.5	4	2	grams/min
Addition Time	1	22	44	Minutes
Number of Washes	#	#	2	
Entrained Solids	#	#	0.402*	Grams
Precipitation Yield	99.8	99.5	99.4	%
Solids Volume	250	161	152	MI
Nitrate in Wash	#	#	7890*	Ppm
Particle Size (mean)	76	113	130	Microns
Particle Size (std dev)	70	50	62	
% <15.56 micron	23.95	3.53	3.96	%

\* Dip tube slipped down below 181 ml during decanting of spent precipitant.

# Run was aborted prior to washing.

### Conclusions

The proposed flowsheets shown in SRT-AMC-99-0099 were verified by the lab-scale tests and will be utilized with minor modifications for the full scale demonstration tests.

The modifications are:

- Maintain the feed solution at 1M nitric acid during dilute feed processing.
- During recovery from inadvertent addition of 0.1M oxalic acid in place of 8 wt% oxalic acid, the solution should be adjusted to 1M nitric acid prior to addition of solid oxalic acid and the oxalic acid should be slowly added over 44 minutes.

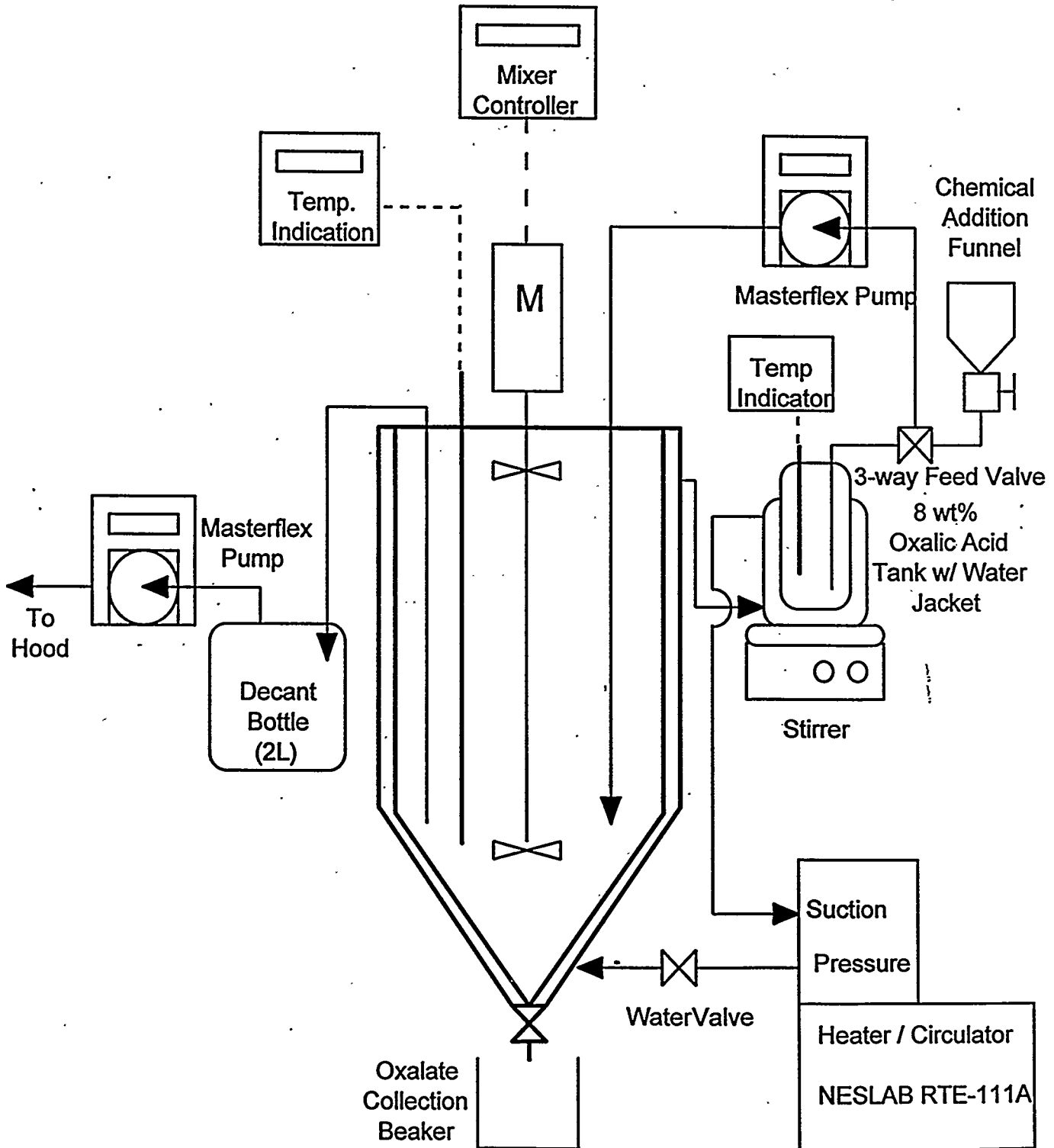
## REFERENCES

1. Task Technical and QA Plan, WSRC-RP-99-0610, July 12, 1999.
2. M. E. Stone, AM/CM Surrogate Makeup Sheet (U), SRT-AMC-98-0088, Revision 1, October 28, 1998.
3. J. E. Marra, et al. Americium-Curium Stabilization – 5' Cylindrical Induction Melter System Design Basis (U), SRT-AMC-99-0001, January 15, 1999.
4. M. E. Stone, Checkout Plan for Lab-Scale Precipitation Tests (U), SRT-AMC-99-0168, August 24, 1999.
5. M. E. Stone, Calculations for Lab-Scale Precipitation Tests (U), SRT-AMC-99-0169, August 25, 1999.
6. M. E. Stone, Experimental Plan for Lab-scale Precipitator (U), SRT-AMC-99-0171, August 26, 1999.
7. M. E. Stone, Baseline Run Plan for Lab-Scale Water-Jacketed Precipitator (U), SRT-AMC-99-0188, September 7, 1999.
8. M. E. Stone, Run Plan for Processing 50% Diluted Surrogate Feed (U), SRT-AMC-99-0193, September 20, 1999.
9. M. E. Stone, Run Plan for Processing 50% 1M Nitric Acid Diluted Surrogate Feed (U), SRT-AMC-99-0195, September 20, 1999.
10. M. E. Stone, Run Plan for Processing 33% Diluted Surrogate Feed (U), SRT-AMC-99-0197, September 21, 1999.
11. M. E. Stone, Run Plan for Processing 25% Diluted Surrogate Feed (U), SRT-AMC-99-0198, September 22, 1999.
12. M. E. Stone, Run Plan for Processing 50% Diluted Surrogate Feed w/ Baseline Oxalic Acid Flowrate (U), SRT-AMC-99-0199, September 23, 1999.
13. M. E. Stone, Run Plan for 50% wt% Nitric Acid Addition with Lanthanum Oxide Recovery (U), SRT-AMC-99-00200, September 28, 1999.
14. M. E. Stone, Run Plan for 0.1M Oxalic Acid Addition with Solid Oxalic Acid Addition (U), SRT-AMC-99-00202, September 28, 1999.
15. M. E. Stone, "Run Plan for 0.1M Oxalic Acid Addition with Nitric Acid and Solid Oxalic Acid Addition (U), SRT-AMC-99-00207, October 25, 1999.
16. WSRC-NB-99-00109, Coupled Precipitator Two and Scoping Non-Baseline Precipitations Laboratory Notebook.
17. Manual L27 Procedure 2.07, Am/Cm Labscale Water-Jacketed Precipitator Operation



ATTACHMENT ONE: LABORATORY EQUIPMENT SETUP

LABSCALE PRECIPITATOR EQUIPMENT SETUP



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