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Demonstration of Disposal of Americium and Curium Legacy Material Through High Level Waste System:

Results from Baseline, Nitrate Added Flowsheet Studies

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List of Abbreviations

ADS	Analytical Development Section
Am	Americium
Cm	Curium
DF	Decontamination Factor (= starting concentration/ending concentration)
DU	Depleted Uranium
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
MnO_4^-	Permanganate
MST	Monosodium Titanate
NaOH	Sodium Hydroxide
Np	Neptunium
Pu	Plutonium
SRTC	Savannah River Technology Center
U	Uranium
WPTS	Waste Processing Technology Section

1.0 Executive Summary

This report details the results of a demonstration for disposal of the legacy solution containing americium and curium through the High Level Waste system. This experiment (#8) simulates the variation on the baseline disposal process that adds sodium nitrate as a means of reducing the rate of hydrogen generation from radiolysis. These initial studies examined actinide removal efficiency and rheology of the resulting slurry. While the studies continue on several mitigation pathways, data is presented to inform the reader of the most current results for this experiment.

Upon addition of caustic and sodium nitrate to the acidic legacy solution, the vast majority (99.99%+, by ICP-MS) of the curium precipitates from solution. Radiochemical analysis indicates that the remaining supernatant liquid possesses sufficient alpha activity to require another ~6 fold reduction in the total concentration of alpha emitters to meet Saltstone requirements. This represents lower actinide removal efficiency upon neutralization than achieved with the baseline process demonstrations. Under the conditions of the demonstrations, the baseline experiments only marginally satisfied the Saltstone waste acceptance criteria. Therefore, we recommend continuing this demonstration through the entire process sequence.

The rheology of the slurry from this experiment does not differ markedly from that of the baseline process.[13] Simplified flow experiments indicate little tendency for the solids to settle and deposit at low flow rates. This testing also indicated that replacing the depleted uranium and sodium nitrate with manganese nitrate produces a slurry with very adverse rheology.[13]

This process chemistry appears viable for treatment of the legacy solution in a manner that mitigates concerns for transfer, hydrogen generation, and actinide solubility. Completing the demonstration through the full process simulation will provide a more complete technical basis for implementation.

2.0 Introduction

Tank 17.1 in F-Canyon contains an americium and curium loaded solution. The Am/Cm components of this solution resulted from the Mk 40 and Mk 41 campaigns during the mid/late 70's.[1] Since 1984, no further additions to Tank 17.1 occurred except to replace evaporative losses.[2] In 1993, DOE-SR requested WSRC to evaluate proposed disposition options and provide a recommended disposition option.[3] More recently, an evaluation identified the most cost-effective method as discarding this material directly to the High Level Waste tanks.[4] However, a recent risk assessment identified a primary risk of this method as the potential dissolution of curium into solution, where it could impact several

HLW processes.[¥] Given the high specific activity (80.9 Ci/g) and energy of ^{244}Cm emmitted alpha particle (5.8 MeV/discharge), the soluble curium concentration during the disposal process proves key in determining whether the resultant waste meets disposal requirements. Limited data exists on curium solubility in highly alkaline solutions [5,6,7,8] and hence the program required additional experimental measurements.[9]

This document details the baseline, nitrate added (Experiment #8) flowsheet results of the investigations designed to determine whether the curium containing waste stream causes problems to HLW operations. This experiment is a derivitive of the original baseline experiments in that extra nitrate is added to the slurry. The extra nitrate reduces the hydrogen generation and brings it closer to acceptable limits.[14,15] This experiment examines whether the added nitrate alters the amount of actinide that precipitates during the neutralization of the solution and examines the fluid properties of the slurry for transfer. SRTC also considered using manganese nitrate in the place of DU, but due to unfavorable rheology (see section 4.3) this pathway was not pursued. This interim report does not contain the results from other experiments; a final document containing all the experimental data will be issued at a later date.

3.0 Experimental Detail

Figure 1 provides a schematic of the proposed disposal path for the legacy solution. The baseline, nitrate added flowsheet dilutes the sludge by adding depleted uranium (DU) [10] to help make the sludge more similar to the sludge already present in HLW. For this particular demonstration, addition of 50 wt % NaOH solution, 40 wt % $NaNO_3$ solution, and dilution water occurs in sufficient volume to produce a resultant slurry with 1.2 M free hydroxide and 3.3 M in nitrate. Personnel will transfer the slurry first to F-Tank Farm and then to Tank 51H via an interarea transfer line. “Inhibited water” (i.e., 0.01 M NaOH solution) and sludge from Tank 7F will follow or accompany the transfers to help scour the high activity solids from the transfer piping.

If warranted, based on measurements from the neutralized solution, the program will continue the demonstration through the balance of the disposition plan. After holding the waste in Tank 51H for some period, personnel will wash the sludge contained in Tank 51H to meet the requirements for feed material to the Defense Waste Processing Facility (DWPF).[11] Decanted liquid and wash water will pass through an evaporator after mixing with supernatant waste in an as yet unidentified tank. Eventually, the decanted liquid waste will pass through the Salt Processing Facility with treatment by addition of monosodium titanate (MST) to remove soluble strontium and radionuclides that emit

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[¥] While the americium-243 present also represents a source term danger, the dose proves small in comparison to that of curium-244 present.

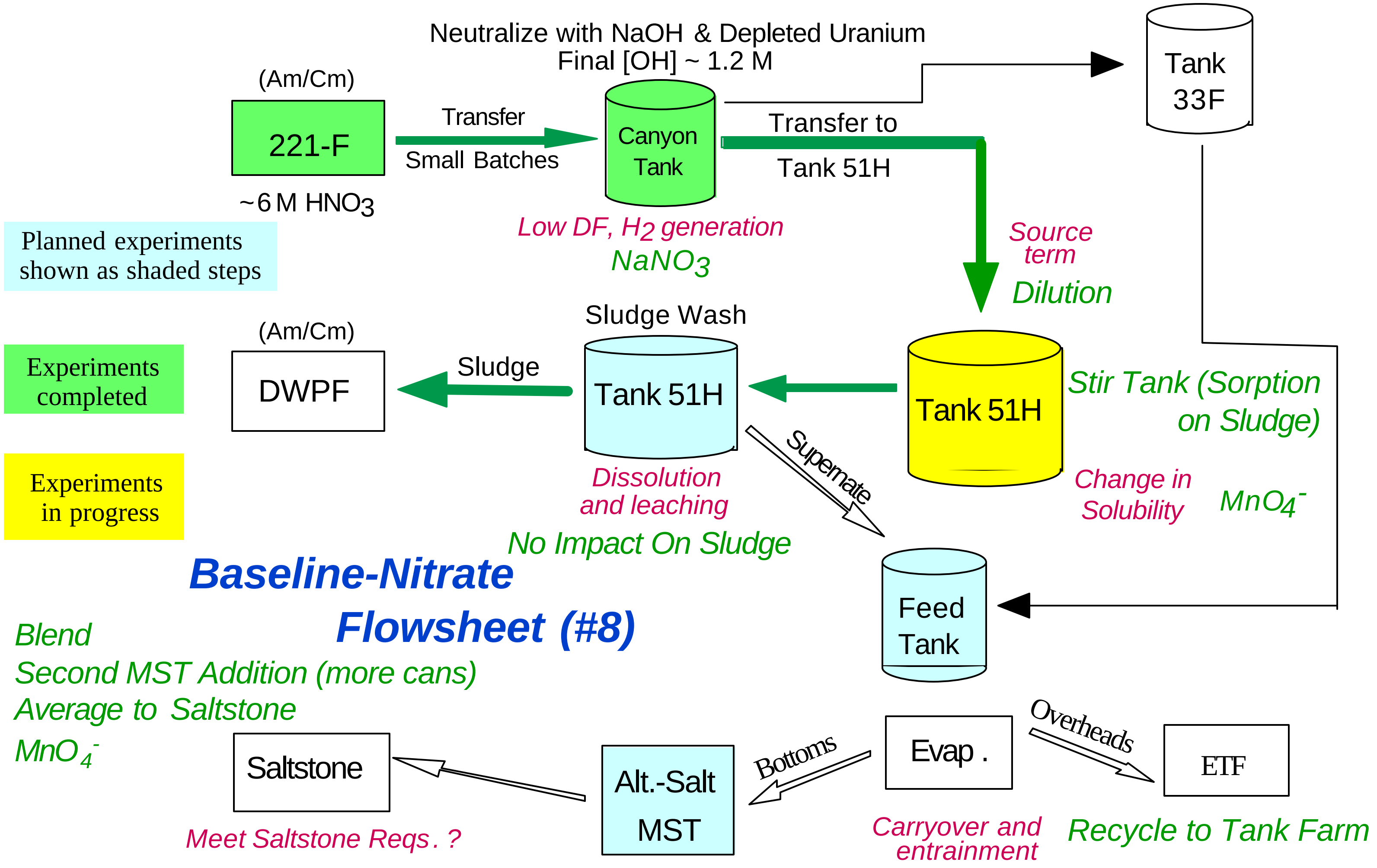

Figure 1. Proposed path for disposal of legacy material in Tank 17.1 of Building 221-F. The experiments of this demonstration examine the proposed path plus a number of variants. The color coding shows the approximate progress on the baseline demonstration at the time of this report.

alpha radiation. Disposition of the washed solids in Tank 51H occurs via vitrification in DWPF.

This document details the baseline, nitrate added experiment (#8) which, of all eight experiments, is the one most favorable for meeting the HDB-8 hydrogen generation limit.

4.0 Results of Investigations

F-Canyon Operations personnel provided 100 mL of Tank 17.1 solution to SRTC for the investigations. We analyzed this material as received and previously reported some of the results.[12]

While the curium content of the supernatant liquids is a concern (^{244}Cm is by far the largest contributor to the radioactive decay activity in these waste supernates), the greater concern is to insure the total alpha reaches, and remains below the Saltstone limits of 18 nCi/g. For this reason, this report deals mainly in terms of total alpha activities, instead of curium concentrations.

4.1 Analytical Limitations

The solutions used in these experiments represent a challenge to ADS for three reasons:

- low curium concentration
- high salt content
- high gamma activity relative to alpha activity

The high salt content interferes in getting consistent readings of curium by counting methods. The high salt content also interferes with ICP-MS by requiring larger sample dilutions. The larger dilutions can dilute trace elements in the sample, to below detection limits.

The high gamma content interferes with the total alpha readings, and biases them high. Due to this, the total alpha results for most of the samples are upper bounds. However we conservatively use them as reported.

4.2 Neutralization of the Acidic Tank 17.1 Solution

For Experiment #8, personnel followed the same general neutralization procedure as used in previous studies.[12] The ratios of materials for the neutralizations were derived from guidance provided by Loftin.[10] The baseline neutralization uses the following materials in the following recipe.

1 volume of depleted uranium solution (350 g/L of ^{238}U)
1.35 volumes of Tank 17.1 solution
5.64 volumes of 40 wt % $NaNO_3$ solution

1.57 volumes of 50 wt % NaOH solution
4.38 volumes of process water

For comparative purposes, Experiment #1 and #2 used the following recipe:

1 volume of depleted uranium solution (350 g/L of ^{238}U)
1.39 volumes of Tank 17.1 solution
1.85 volumes of 50 wt % NaOH solution
9.72 volumes of process water

In the canyon, personnel will add the Tank 17.1 contents to the DU solution, followed by addition of the $NaNO_3$ solution, the NaOH solution, and finally the dilution water. Due to volumes of the available tanks, the neutralization will occur in 10 batches. The SRTC experiments used the same ratio and order of addition, but due to the small amount of material, we neutralized the material for each experiment in one batch. In each of the neutralizations, we allowed the slurry to stir and cool before gravity settling the solids. After settling, personnel pulled supernate samples and filtered through 0.2 μm poresize nylon membrane syringe filters. We submitted filtrates to ADS for analyses. Table 1 lists the results obtained for the filtered samples. Data from Experiments #1 and #2, and the original acid solution is provided for comparison.

Table 1. Comparison of Tank 17.1 Material to Neutralized Slurries (Filtered Supernates)

Analysis	Original Solution	Experiment #1	Experiment #2	Experiment #8
Counting (nCi/g)				
Total Alpha	1.17E+07	6.47E+01	8.97E+01	1.16E+02
^{244}Cm	1.15E+07	1.88E+01	2.69E+01	2.21E+01
^{238}Pu	8.61E+04	2.65E+00	4.07E+00	5.94E-01
$^{239/240}$Pu	3.02E+04	8.15E-01	1.12E+00	3.51E-01
^{241}Pu	= 4.61E+03 (DL)	= 1.07E+00 (DL)	= 1.19E+00 (DL)	= 1.43E+01 (DL)
^{137}Cs	1.15E+05	9.66E+03	1.17E+04	1.57E+04
Rad ICP-MS				
mass 238 (mg/L)	909	8.62	8.56	15.2
^{239}Pu (nCi/g)	1.88E+02	1.65E-01	1.92E-01	= 5.71E-02 (DL)
^{240}Pu (nCi/g)	2.26E+04	9.93E-01	8.27E-01	7.23E-01
mass 241 (mg/L)	38.4	= 0.00190 (DL)	= 0.00190 (DL)	= 0.00190 (DL)
^{243}Am (nCi/g)	1.27E+05	= 3.44E-01 (DL)	= 3.44E-01 (DL)	= 3.44E-01 (DL)
^{244}Cm (nCi/g)	1.10E+07	= 1.40E+02 (DL)	= 1.40E+02 (DL)	= 1.40E+02 (DL)
Free Acid (M)	5.97	*NA*	*NA*	*NA*
Free Hydroxide (M)	*NA*	1.40	1.58	0.805

Ion Chromatography (M)				
NO_3^-	6.37	*NA*	*NA*	3.73
NO_2^-	= 2.17 (DL)	*NA*	*NA*	0.0268
SO_4^{2-}	= 0.521 (DL)	*NA*	*NA*	0.0187

(DL) refers to "Detection Limit", "*NA*" refers to "not applicable"

The concentration of ^{244}Cm by counting derives, as a percentage of total alpha emissions. At this time, we suspect that that the observed wide variation in the ^{244}Cm activity results from the matrices. Studies continue to improve the ^{244}Cm measurements. In every analysis, the concentration of ^{244}Cm by ICP-MS proved less than the detection limit. We assumed the concentration as equal to or less than the detection limit for the purposes of Table 2. This means the DF values for the ICP-MS represent lower bounds. A careful reader will note that the total alpha value (for the counting type analysis) is greater than the sum of the listed alpha emitters. For clarity, we have not reported every alpha emitter present.

Table 2. Decontamination Factor (DF) results for the Neutralizations

Sample	Total-Alpha DF	^{244}Cm (counting) DF	^{244}Cm (ICP-MS) DF
Experiment #1	181,000	612,000	= 78,900 (DL)
Experiment #2	130,000	428,000	= 78,900 (DL)
Experiment #8	101,000	520,000	= 165,000 (DL)

4.3 Rheology Experiments

Both Canyon and HLW personnel had concerns about the ability of high-nitrate slurries being too viscous to flow well enough. The Immobilization Technology Section was asked to characterize four basic slurries for the Americium-Curium (Am/Cm) flowsheet

Figure 2. The four simulant slurries; baseline, 3.3 M nitrate, 3.85 M nitrate, manganese

studies. Three Am/Cm simulant slurries were prepared at three nitrate levels, all containing depleted uranium. The fourth slurry was an Am/Cm slurry that contained manganese as a substitute for depleted uranium.

Rheological testing occurred in radioactive and nonradioactive lab hoods. The samples containing depleted uranium were each tested under identical testing conditions. The sample containing manganese was tested multiple times in an attempt to understand its rheological behavior. The rheological data was fit to the Bingham Plastic fluid model. The table below summarizes the results.

Table 3. Summary of Bingham Plastic Fluid Parameters

Sample	Yield Stress, dynes/cm^2	Consistency, cP	R^2	Density, g/ml
Baseline Slurry #	0.90	1.81	0.9936	1.12
3.3 M Nitrate	4.15	3.38	0.9939	1.21
3.85 M Nitrate	5.27	3.90	0.9945	1.23
Manganese &	67.9	4.81	0.9796	1.27

The baseline is 0.79 M in nitrate & The manganese is 3.85 M in nitrate

With the DU containing slurries, as the nitrate content increased, so did the viscosity and density. With the manganese test, the slurry was far more viscous than in the DU cases.

For the purposes of showing relative flow characteristics, SRTC conducted an additional test, using a condenser column with a spiral cooling coil (Figure 3).

Figure 3. The Slurry "racetrack"

Using 30 mL of each of the slurries, we timed how long it took for the whole amount to go through the glass column. Each slurry was well mixed before pouring into the column. Each slurry run was done in duplicate, and the column was cleaned between each run.

Sample	Time (s)
Baseline	5.6
3.3 M Nitrate	5.9
3.85 M Nitrate	6.3
Manganese	> 480 (est.)

For the DU slurries, the time to pass through the column was about the same, with the time increasing as the nitrate content increased. In the case of the manganese slurry, four minutes had passed by the time the slurry front had reached about halfway through the column. While this is not a rigorous test, it does illustrate the relative flow characteristics of each of the slurries. In this case, the manganese shows extremely poor flow.

For a more detailed explanation of the rheology data, refer to the full report.[13]

4.4 Overview of Experiment #8.

While the title of this report would indicate a preoccupation with curium removal, the real goal of this project is to reduce the total alpha emissions to a level under the Saltstone limit of 18 nCi/g. At this point in the lifecycle of Experiment #8, another ~6 fold reduction in total alpha will be required to meet the Saltstone limits (Table 4).

Table 4. Post-Neutralization Supernates - Required Additional DF to Meet Saltstone.

Analysis	Experiment #1	Experiment #2	Experiment #8
Total Alpha	6.47E+01	8.97E+01	1.16E+02
Saltstone Limits (nCi/g)	18	18	18
Required Additional DF	3.59	4.98	6.44

Ultimately, due to the chemical and dilution operations of the remaining steps of the sludge lifecycle, SRTC estimates the total alpha activity will be reduced to within, or close to, Saltstone limits. This represents lower actinide removal efficiency upon neutralization (based off of one data point) than achieved with the baseline process demonstrations. Under the conditions of the demonstrations, the baseline experiments only marginally satisfied the Saltstone waste acceptance criteria. Therefore, we recommend continuing this demonstration through the entire process sequence. In any case, if one were to use the real dilutions that will occur, SRTC estimates that the total alpha will fall well within the Saltstone limits by the end of sludge processing. SRTC also sees no effect of curium solubility from the extra nitrate, but this judgement is from a single data point.

4.5 Future Work

The Am/Cm slurry in Experiment #8 has not progressed through the full lifecycle as some of the other Experiments have. Future work for Experiment #8 will entail aging in a Tank 51/7 slurry surrogate, washing with inhibited water, and conducting the MST strikes. It should be noted that in the case of the aging step, a new Tank 51/7 slurry surrogate will be needed as all of the previous material has been consumed.

5.0 Conclusions

Experiment #8 demonstrates a total alpha DF on the order of 10^5 upon neutralization. Analyses for ^{244}Cm and total alpha compare well to the previous baseline experiments (#1-2). All the work to date indicates that curium, once precipitated by caustic addition according to canyon procedures, shows a minimal propensity to subsequently dissolve during dilution or due to changes in solution composition. While testing continues, this initial data suggests minimal concern with disposal of the legacy material to the High Level Waste system. Elevated levels of nitrate have so far exhibited no effect on curium solubility.

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